

Phases of Matter and Phase Transitions; From Mean Field Theory to Critical Phenomena

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Abstract

This paper is the second in a series[1] that looks at the theory of the phases of matter from the perspectives of physics and the philosophy of science. The first paper considered the question of how can matter, ordinary matter, support a diversity of forms. We see this diversity each time we observe ice in contact with liquid water or see water vapor (steam) come up from a pot of heated water. These differences have been apparent to humankind for millennia, but only brought within the domain of scientific understanding since the 1880s. By 1937 a variety of roughly similar theories, going under the name “mean field theory” described how the average forces in materials produce the different phases.

Materials can undergo discontinuous jumps from one phase to another, which are called *first order phase transitions*. By adjusting the parameter which control the phases, one can often make the jumps arbitrarily small and thus produce *continuous phase transitions*. In the years between 1937 and 1971, scientists recognized that the continuous phase transitions must be described not by average forces but by fluctuations away from the average. An entirely new approach, the *renormalization group theory*, was developed to deal with this situation. This theory was then applied to problems in particle physics and several other areas.

Both kinds of phase transitions are abrupt changes in the equilibrium behavior of the materials. These changes only occur abruptly because the materials around us can be considered to be made up of an effectively infinite number of particles. The paper follows the arguments and theories which use this infinity to describe the behavior of real, finite, materials.

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1 Introduction

1.1 Condensed Matter Physics

The discipline of physics has many different goals. One goal, and certainly not the least important, is to provide intellectual bridges among the different theories describing the many different domains of natural behavior. Thus Newton's gravitational theory is equally applicable to an apple and the moon. Electromagnetic theory describes semiconductor devices, nuclear spins, and starlight. Nuclear physics encompasses stellar energy production. The subject which bears the name "condensed matter physics" is in large measure concerned with bridging the gap between the theory of the microscopic behavior of atoms, electrons, and ions and the observed macroscopic behavior of bulk matter.

The forces and fields which surround microscopic particles act to produce the range of different thermodynamic *phases* observed in the materials we see about us. The phases are different states of aggregation with qualitatively different properties, which then lead to structures which are amazingly diverse and beautiful. Water, for example, can exist in several different thermodynamic phases depending upon the thermodynamic conditions around it. Three of the phases are illustrated in Figure (1) that shows a snowflake (a crystal of a solid phase of water) and a splashing of the liquid phase. A third phase of water, the low density phase familiar as water vapor or steam, exists in the empty-looking region above and around the splashing liquid.

Different phases of matter have qualitatively different properties. As you see, ice forms beautiful crystal structures. So do other solids, each with its own characteristic shape and form. Each crystal picks out particular spatial directions for its crystal axes. This occurs because of forces and interactions produced by the interactions of the microscopic constituents of the crystals. Crystalline materials are formed at relatively low temperatures. At these temperatures, microscopic forces tend to line up neighboring molecules and thereby produce strong correlations between the orientations of close neighbors. Such correlations extend through the entire material, with each molecule being lined up by several neighbors surrounding it, thereby producing an ordering in the orientation of the molecules that can easily extend over a distance a billion times larger than the distance between neighboring atoms. This orientational order thus becomes visible in the macroscopic structure of the crystal, as in Figure (1), forming a macroscopic manifestations of the effects of microscopic interactions.

The same materials behave differently at higher temperature. Many melt and form a liquid. The long-range orientational order disappears. The material gains the ability to flow. It loses its special directions and gains the full rotational symmetry of ordinary space.

Many of the macroscopic manifestations of matter can be characterized as having *broken symmetries*. Phases other than simple vapors or liquids break one or more of the characteristic symmetry properties obeyed by the microscopic interactions of the constituents forming these phases. Thus, a snowflake's outline changes as it is rotated despite the fact that the molecules forming it can, when

isolated, freely rotate.

Then too, the alignment of atomic spins or electronic orbits can produce diverse magnetic materials, including ferromagnets, with their substantial magnetic fields, and also many other more subtle forms of magnetic ordering. A crystal in which the magnetization can point in any direction in the three-dimensional space conventionally labeled by the X, Y, and Z axes is termed an “XYZ” ferromagnet. Another kind of ferromagnet is called an “XY” system, and is one in which internal forces within the ferromagnet permit the magnetization to point in any direction in a plane. The next logical possibility is one in which there is a selected axis of magnetization, and the magnetization can point either parallel or antiparallel to that axis. A simple model describing this situation is termed an Ising model, named after the physicist Ernest Ising[2], who invented it in conjunction with his adviser Wilhelm Lenz[3, 4]. We shall, below, consider in some detail the behavior of this Ising model and its transition from an ordered, ferromagnetic state, to a disordered one in which the magnetization is precisely zero.

Some of these special properties of special thermodynamic phases are of everyday importance. Our economic infrastructure is, in large measure, based upon the various phase-dependent capabilities of materials to carry electrical currents: from the refusal of insulators, to the flexibility of semiconductors, to the substantial carrying capacity of conductors, to the weird resistance-free behavior of superconductors. This flow, and other strange properties of superconductors, are manifestations of the subtle behavior of quantum systems, usually only seen in microscopic properties, but here manifested by these materials on the everyday scales of centimeters and inches. I could go on and on. The point is that humankind has, in part, understood and used these different manifestations of matter, manifestations that go under the name “thermodynamic phases”. This article is a brief description of the ideas contained in the science of such things.

1.2 Order parameters

A previous publication[1], hereafter denoted as paper I, describes the development of the theory of phase transitions up to and including the year 1937. In that year Lev Landau[5] put together a theoretical framework that generalized previously existing mean field theories of phase transitions. In Landau’s approach, a phase transition is seen in the breaking of a mathematical symmetry which manifests itself in the behavior of an *order parameter* describing the state of the material. When two different phases are in contact, one can distinguish between them by defining them to have different values of a physical quantity which is often called an *order parameter*. For example, in a ferromagnet the order parameter is the vector magnetization of the material. Since the spins generate magnetic fields, this alignment is seen as a large time-independent magnetic field vector, pointing in some particular direction. The order parameter in this example is then the vector describing the orientation and size of the material’s magnetization and its resulting magnetic field.

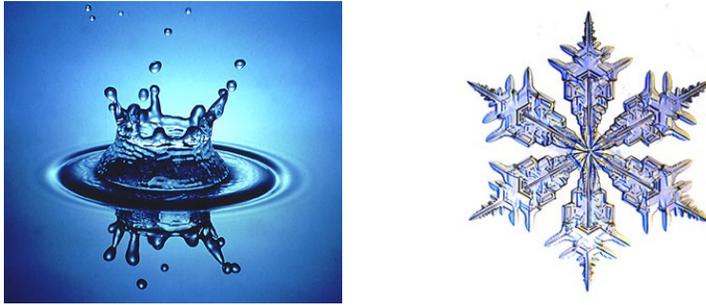


Figure 1: Splash and snowflake. This picture is intended to illustrate the qualitative differences between the fluid and solid phases of water. On the left is liquid water, splashing up against its vapor phase. Its fluidity is evident. On the right is a crystal of ice in the form of a snowflake. Note the delicate but rigid structure, with its symmetry under the particular rotations that are multiples of sixty degrees.

Other order parameters describe other situations. A familiar order parameter characterizes the difference between the liquid and the vapor phases of water. This parameter is simply the mass density, the mass per unit volume, which takes on larger values in the liquid phase and smaller ones in the vapor phase. Thus, water expands as it boils. In the superfluid examples, the order parameter is a complex quantity, describing the wave function of the condensed state, with a square that is proportional to the mass density of particles within that state.

1.2.1 Phase diagrams, phase transitions, and singularities

Condensed matter physics is concerned with identifying and classifying these different phases of matter, both for their intrinsic interest and for their potential practical importance. As the environment around the materials is changed, for example by varying the temperature or pressure, the systems undergo what are called a *phase transition*, that is the change from one state of matter into another. Figure (2) shows a simple example of a *phase diagram*, a picture which indicates where the phase transitions occur relative to the variables which describe the material's environment. This diagram applies to Ising's ferromagnet in two or more dimensions. There are two variables describing the environment, the temperature, forming the x-axis, and the magnetic field in the direction of the axis of magnetization, forming the y-axis.¹

¹We use the symbol H to describe this field. This symbol is traditionally used for the magnetic field applied to a material from outside itself[6]. The symbol B is then used to describe the total (averaged) field within the material, the field from outside added to an averaged field within the material. The use of B and H is an example of the application of mean field theory[1]. This approximation is quite successful whenever the sample under study are large enough to contain a huge number of charged particles.

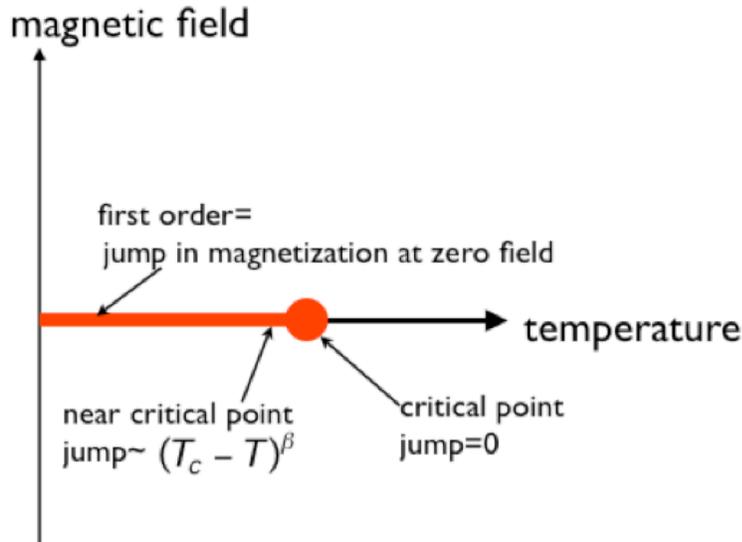


Figure 2: Phase diagram for a ferromagnet. The case depicted is one in which the magnetization can point in one of two possible directions, diametrically opposed to one another. The y -axis is the magnetic field applied to the material from outside, taken as pointing in one of these two directions. The heavy line segment is at zero magnetic field, and includes temperatures lower than the critical temperature, T_c . Along this line segment there is a first order phase transition. The magnetization is positive above this line segment, and negative below. As the magnetic field passes through zero along this segment, the magnetization goes through a jump by changing sign. This jump is the first order phase transition. The heavy dot at the end of the line indicates a continuous phase transition. The location of such a transition is called a *critical point*. At zero magnetic field and temperatures above this critical point the magnetization is strictly zero. The jump has disappeared. The point of disappearance at T_c is the place where there is a continuous phase transition.

The important characteristic of the ferromagnetic materials is that they can often support a very strong magnetic field. For this reason, materials from the lodestones known to the ancients to modern iron have important practical applications based upon their very strong magnetic properties. This characteristic arises precisely because neighboring atoms tend to align their spins and their magnetic moments. Thus a small applied magnetic field is strongly enhanced by the behavior of the material itself. The enhancement is larger at low temperatures and smaller at high temperatures. The higher temperatures tend to literally shake up the aligned spins and substantially reduce their alignment. For temperatures above the critical temperature, when the field is zero; the alignment is also zero. However there is a qualitative change in behavior on the zero field line when the temperature passes below the critical temperature. (This temperature is indicated as T_c on Figure (2).). Below the critical temperature, the spins are always aligned, even at zero field. At these temperatures, if the field is even slightly positive, the magnetization is substantially positive; if the field is ever so slightly negative, the magnetization remains substantial and points in the opposite direction. Thus there is a discontinuous jump in the magnetization as the field passes through zero whenever the temperature is smaller than T_c . A discontinuous jump in thermodynamic behavior is indicative of what is called a *phase transition*.

The theory of phase transitions was first developed by J. Willard Gibbs[9, 10], a late Nineteenth Century American scientist, who produced a definitive discussion of the subject called *thermodynamics*. Despite its name, thermodynamics is largely concerned with the time-independent behavior of bulk matter. If a piece of matter is left in a constant environment over a long period of time, it can settle into an unchanging behavior called *thermodynamic equilibrium*. The state of the system in equilibrium depends upon parameters that describe its environment, for example temperature and pressure. Gibbs saw that the equilibrium behavior could include the properties of the many different phases of matter. He then defined a phase transition to be any abrupt change singularity in the thermodynamic properties of the system as the environmental parameters are varied. In mathematics a singularity is the word used to describe an abrupt change in a mathematical function. This mathematical concept will have many profound implications for the description of phase transitions. A discontinuous jump in the most fundamental thermodynamic quantities is called a *first order phase transition*, while a more subtle change is termed a *continuous phase transition*. Gibbs' thermodynamic studies gave us a definitive treatment of the qualitative behavior of phase transitions.

1.2.2 From van der Waals to Landau

The magnetization jump has its parallel in the jump in mass density, mass per unit volume, which occurs in a liquid gas phase transition, which has a phase diagram rather similar to that of Figure (2). and van der Waals[12] focused upon this density jump in density in the liquid-gas phase transition. They worked with the experimental data of

Using the data of Thomas Andrews[13], Johannes van der Waals developed an approximate equation describing the dependence of the fluids' pressure upon temperature and density. This was soon augmented by James Clerk Maxwell's[11] thermodynamic theory of the jump. Overall the van der Waals equation was quite successful. It gave a qualitatively accurate picture of the phase diagram.

There were, of course, deviations between the simple theory and the actual behavior. For many years, van der Waals worked to reduce these deviations by gaining a better understanding of molecular forces and by putting together a more detailed and accurate theory. One discrepancy between theory and experiment caused him particular distress. One might hope that the jump in density near the critical point, i.e. the position of the continuous phase transition, might have a particularly simple dependence upon a parameter like temperature, T . The jump is particularly small in this region and one might think that might give it a simple dependence upon the temperature difference from the critical point, described by a variable $T - T_c$, where T_c is the critical temperature. In fact, the van der Waals theory predicted a cubic equation for the density in this region, and a simple result in this region:

$$\text{jump in density} = \text{constant} \times (T_c - T)^\beta \quad \text{with} \quad \beta = 1/2 \quad (1)$$

Numbers like β appearing as exponents in power laws describing near-critical behavior are called *critical indices*. According to the power law in Eq. (1) the jump in the order parameter approaches zero as the critical point is approached. Andrews' data indeed does show this behavior, and close to criticality it fits a power law as in Eq. (1). But the value for the critical index in the experimental data is much closer to one third than to van der Waals' one half[15]. This discrepancy will play a very important role in what follows.

The previous paper, *I*, traces in detail the nature and impact of impact of van der Waal's theory. The theory assumes that the molecules in a fluid feel the average of the forces produced by the other molecules. A theory of this nature is called a mean field theory. Over his career, van der Waals used mean field theory to predict the variation of fluid density with pressure and temperature for a wide variety of pure and mixed fluids. Following rather soon after van der Waals, Pierre Curie[16] and Pierre Weiss[17] derived a theory of ferromagnetism based upon the same ideas. Many other workers examined other phase transition, understood their various order parameters and the forces which drive them and developed appropriate mean field theories of the resulting transitions. In each case the theories assumed that the transition could be understood in terms of the average forces and interactions among the microscopic constituents. The different papers in these different areas of condensed matter physics were all concerned with finding appropriate approximate equations describing how the order parameters varied as the environmental conditions of the materials were varied.

Landau in his 1937 work[5] generalized the work of van der Waals, Pierre Curie, and Paul Ehrenfest[18] and followed them in noticing a deep connection

among different phase transition problems[19]. Starting from the recognition that each phase transition was a manifestation of a broken symmetry, he used the order parameter to describe the nature and the extent of symmetry breaking[5].

Landau wrote an expression for a thermodynamic quantity, the free energy, as a function of the order parameter. He worked near the critical point, so that he could simplify his expression by assuming that the order parameter was small. He then used the symmetries of the order parameter to further limit the possible behaviors of the free energy. In the simplest case, the result he found depended upon two environmental parameters, those used in the magnetic case discussed above. One parameter $t = 1 - T_c/T$ measures the deviation from the critical temperature, while the other, h , the analog of the ferromagnet's applied magnetic field, measures the extent of the symmetry breaking by external fields. Landau then calculated an equation for the order parameter by using the thermodynamic result that the free energy is minimized in thermodynamic equilibrium. In calculating the value of the order parameter which would produce such a minimum, he found a cubic equation for the order parameter. This equation could be specialized to the case in which there is no external symmetry breaking. His equation predicted a jump in the order parameter of the form of Eq. (1), with once more the value $\beta = 1/2$.

1.3 Away from corresponding states— Toward universality

Landau's calculation represented the high water mark of the class of theories described as "mean field theories". He showed that all of them could be covered by the same basic calculational method. They differed in the symmetries of the order parameter, and different symmetries could give different outcomes. However, within one kind of symmetry the result was always the same. This outcome was very pleasing for many students of the subject, particularly so for the physicists involved. We physicists especially like mathematically based generalizations and Landau had brought in an elegant generalization, which simplified a complex subject. The idea that different fluids have almost identical relations between their pressure temperature and density is called the "principle of corresponding states."

This ideas had broad support among the scientists working on phase transitions. Starting with van der Waals, continuing with Einstein[20], George Uhlenbeck, and later on E. A. Guggenheim[21], work on phase transitions was inspired by the aim and hope that all fluid's phase diagrams would be essentially alike. However, Landau's work marked a new beginning. His method would apply only near a critical point and his version of corresponding states could be expected to apply only in this region. So Landau deepened the theory but implicitly also narrowed its domain of application to a small region on the phase diagram. This was the start of a new point of view, which we shall see develop in the rest of this paper. The new point of view would come with a new vocabulary so that instead of corresponding states people would begin to use the word "universality" a borrowing from an originally Russian word[22].

1.4 Outline of paper

The following section is concerned with bringing the reader up to speed by describing the state of our understanding of phase transitions up through 1937. It starts with a definition of the disciplines of statistical mechanics and ends with summarizing the Landau phase transition theory. In the middle it focuses upon the idea contained in the *extended singularity theorem*, which identifies the abrupt change of a phase transition with a singularity caused by material behavior extended over the entire system. Chapter three details the evidence that shows that mean field theory cannot correctly describe the behavior near the critical point. The development of a new point of view, *renormalization group theory*, is described in the subsequent chapter. Finally, chapter 5 is a selective description of a few of the ideas that developed from consideration of the extended singularity theorem, critical point behavior, and renormalization group theory. It particularly focuses upon how the extended singularity theorem might be applied to a broad class of problems in statistical physics.

2 correlations and spatial structures

2.1 Gibbs' legacy

2.1.1 statistical mechanics

In addition to his extensive studies of thermodynamics, J. Willard Gibbs will be remembered for his careful and elegant formation of statistical mechanics[9]. Thermodynamics describes the equilibrium behavior of matter and sets bounds on the possible non-equilibrium behavior. This science starts by assuming that you know some properties of the matter as given in a basic thermodynamic function. One possible such function is the *free energy function* that expresses the properties of a system with a specified number of particles as a function of its temperature and volume.

On the other hand, statistical mechanics is the science which describes how one calculates the properties of the material system including the free energy function starting from a knowledge of the material's microscopic behavior. The microscopics is usually expressed in terms of a *Hamiltonian* function that gives the system's energy in terms of such basic variables as the momenta and coordinate of its particles. In the Gibbs formulation of statistical mechanics, all thermodynamic quantities, e.g. the free energy, are formed from taking sums of expressions formed from the Hamiltonian over all the different possible configurations of the basic variables.

2.1.2 Averages, fluctuations, and correlations

By forming derivatives of this free energy function one can find all the possible averages of thermodynamic quantities. For example, the average energy can be computed from the free energy and its temperature derivative. Further processes of differentiation generates information about fluctuations from

average values. For example, another derivative of the energy with respect to temperature determines the typical fluctuations in the energy.

It is possible to gain more detailed information. Using Gibbs' prescription to determine the free energy in a situation in which basic parameters like the temperature are taken to be varying with position, one can learn about fluctuations in the energy contained in different regions of the system. Furthermore, one can find out about how the fluctuation in energy in one region is correlated with the fluctuation in another region. Information about both averages and fluctuations will be crucial in our discussions. As we shall see, the theory of first order phase transitions is mostly based on average properties, while the modern theory of continuous transitions depends on understanding fluctuations.

2.1.3 Smoothness versus singularities

In Gibbs' formulation of statistical mechanics, the free energy comes from sums (or sometimes integrals) over configurations. In the usual situation in which everything in the system is quite finite and smoothly varying, the sum has each term proportional to a simple smooth function determined by the number of particles and the energy divided by the temperature. Such a sum² of a finite number of terms is a smooth function of the environmental parameters like temperature, magnetic field, volume, and pressure.

The reader will notice that this smoothness seems to contradict another part of Gibbs' legacy, the statement that a phase transition is a singularity, i.e. failure of smoothness, in some thermodynamic quantity.

This seeming contradiction is the key to understanding much of what happens in phase transitions. No sum of a finite number of smooth terms can be singular. However, for large systems, the number of terms in the sum grows quite rapidly with the size of the system. When the system is infinite, the number of terms is infinite. Then singularities can arise. Thus all singularities, and hence all phase transitions, are consequences of the influence of some kind of infinity. Among the likely possibilities are infinite numbers of particles, infinite volumes, or –more rarely – perhaps infinitely strong interactions. Real condensed matter systems often have large numbers of particles. A cubic centimeter of air contain perhaps 10^{20} particles. When the numbers are this large, the systems most often behave almost as if they had an infinity of particles.

I am going to give a name to the idea that phase transitions only occur when the condensed matter system exhibits the effect of some singularity extended over the entire spatial extent of the system. Usually the infinity arises because some effect is propagated over the entire condensed system, that is over a potentially unbounded distance. I am going to call this result the “extended singularity theorem”, despite the fact that the argument is rather too vague to be a real theorem. It is instead a slightly imprecise mathematical property of real phase transitions³.

²The Ising model free energy involves a sum. For a fluid, integrals must be calculated. For simplicity, I'll call everything a sum.

³Imprecision can often be used to distinguish between the mathematician and the physi-

This phase-transition-singularity-theorem is only partially informative. It tells us to look for a source of the singularity, but not exactly what we should seek. In the important and usual case in which the phase transition is produced by the infinite size of the system the theorem tells us that any theory of the phase transition should look to things which happen in the far reaches of the system. What things? How big are they? How should one look for them? Will they dominate the behavior near the phase transition or be tiny? The theorem is uninformative on all these points.

Sometimes it is very hard to see the result of the theorem. Near a first order phase transition the singularity is very weak. One must use indirect methods to observe it or analyze the singularity. We shall come back to this toward the end of the paper. Conversely, near critical points, singularities are very easy to observe and measure. For example in a ferromagnet, the *magnetic susceptibility*, the derivative of the magnetization with respect to applied magnetic field, is infinite at the critical point. (See Figure (3).)

By looking at simulations of finite-sized Ising systems one can see how the infinite size of the system enters the susceptibility. Figure (3) is a set of plots of susceptibility versus temperature in an Ising system with a vanishingly small positive magnetic field. The different plots show what happens as the number of particles increases toward infinity. As you can see, the finite N curves are smooth, while the infinite- N curve goes to infinity. This infinity is the singularity. It does not exist for any finite value of N . However, as N gets larger, the finite- N result approaches the infinite- N curve. When we look at a natural system, we tend to see phase transitions which look very sharp indeed, but are actually slightly rounded. However, a conceptual understanding of phase transitions requires that we consider the limiting, infinite- N , case.

The reader might wish to note that Gibbs never explicitly made the case that we need an infinite number of particles to get a phase transition. However, the conceptual apparatus that he set up forces us to that conclusion[40].

2.2 Correlations

We have seen a mathematical argument that phase transitions require an infinite system[25]. We shall be most interested in seeing how this argument works itself out in a physical system. A phase transition is a selection process in which a system chooses its thermodynamic phase in a situation in which several choices are equally possible. This choice is extended in space over the entire, in principle infinite, physical system. The manifestation of this choice at two or more points within the system is described by a *correlation* between or among these points. Thus a phase transition is described by a situation in which correlations extend over the entire physical system. The various kinds of behaviors of correlations is described mathematically by an object called the order parameter correlation

cist. The former tries to be precise, the latter sometimes uses vague statements which can then be extended to cover more cases. However, in precisely defined situations, for example the situation defined by the Ising model, the extended similarity “theorem” is actually a theorem[23].

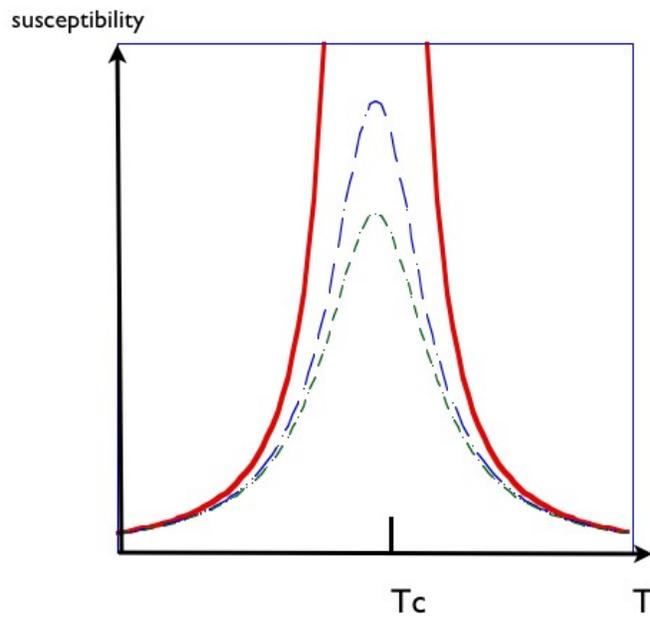


Figure 3: Cartoon view of magnetic susceptibility plotted against temperature for different values of N . The heavy line is shows what happens to the magnetization in an infinite system. The lighter lines apply to systems with finite numbers of particles, with the higher line being the larger number of particles. As N gets larger and larger, the susceptibility becomes more and more peaked. The work of Weiss and Curie show that this plot also applies equally to the derivative of density with respect to pressure in the liquid-gas phase transition.

function. This function describes how the fluctuations in the order parameter, is correlated in different regions of the system. The quantity $g(\mathbf{r}, \mathbf{s})$ describes the correlation between the fluctuations at the two points in space, \mathbf{r} and \mathbf{s} . Mathematically, it is the average of the product of the fluctuations at the two points. In a spatially homogeneous system this correlation function depends only upon the difference between the spatial positions, $\mathbf{r} - \mathbf{s}$. If in addition the system is isotropic, as is for example a fluid, this correlation function only depends upon the distance between the points, $|\mathbf{r} - \mathbf{s}|$.

This function is the most important and useful signal of the situation in the material. In all materials away from a phase transition it dies away at least as fast as an exponential function of the separation distance. For many systems, the large-distance form of the correlation function is roughly given by⁴

$$g(\mathbf{r}, \mathbf{s}) = \text{constant} \times \frac{\exp(-|\mathbf{r} - \mathbf{s}|/\xi)}{|\mathbf{r} - \mathbf{s}|} \quad (2)$$

so that the falloff depends upon the ratio of the distance to ξ . The quantity ξ is called the correlation length. It describes the typical range of spatial correlations in the system.

The extended singularity argument implies that an infinite number of particles should participate in a phase transition. Specifically, we expect them to contribute by producing local changes in the order parameter. On the other hand, a correlation function which drops off as an exponential describes a situation in which local correlations die off with exponential rapidity as they are passed from one part of the system to another. A exponentially rapid die-off, like that in Eq. (2), is inconsistent with a singularity. We expect a slower dropoff, for example that of a power law, to be a signal of a phase transition in process.

For this reason, it would not be surprising if, as a phase transition is approached, the correlation function extended over a larger and larger distance, and if it ended up dropping off more slowly than exponentially at the point of a phase transition.

An extension over a larger spatial extent can be expected to occur via a correlation length that gets larger as the phase transition is approached and then became infinite just at the point of transition. This is, in fact, the behavior observed in a continuous transition.

2.3 Critical Opalescence

Exactly this behavior is seen in the neighborhood of a continuous transition, but not near a first order transition. We shall return to the first order transition below, but for now we concentrate on behavior near the continuous transition.

Observers have long noticed that, as we move close to the liquid gas critical point, the fluid, which hitherto was clear and transparent, turns milky. This

⁴Eq. (2) is the form of the correlation function at large distances given by mean field theory in three dimensions.

phenomenon is called *critical opalescence*. First Marian Smoluchovsky (1908) and then Einstein (1910) studied these fluctuations in statistical systems[24]. Both recognized that critical opalescence was caused by the scattering of light from fluctuations in the fluid's density. They pointed out that the total amount of light scattering was proportional to the spatial integral of the correlation function, g and that the large amount of scattering near the critical point was indicative of anomalously large fluctuations. The heavy line in Figure (3) shows a plot of the temperature dependence of this quantity, which goes to infinity at criticality. In this way, they provided an explanation of critical opalescence. Einstein used his explanation of this physical effect to provide one of his several suggested ways of measuring Avagadro's number, the number of molecules in a mole of material.

The best early detailed theory of critical opalescence was due to Leonard Ornstein and Frederik Zernike[26]. They applied mean-field ideas, derived in part from the work of van der Waals, to the derivation of a correlation function appropriate to a fluid system to a derivation of the form of the correlation function, and particularly to an estimate of the correlation length, ξ . They saw this length diverge on the line of coexistence between the two phases of liquid-gas phase transition as the critical point was approached in the form

$$\xi = \text{constant} \times 1/|t|^\nu \quad \text{with } \nu = 1/2 \quad (3)$$

with t being, once again, the temperature deviation from criticality. Thus the correlation length does go to infinity as the critical point is approached. This result is crucially important to the overall understanding of the critical point. It is a realization of the Gibbs inspired idea that the phase transition, or more specifically criticality, reflects correlations over an infinite region of the system.

Notice that the basic theory equally requires an infinite range of correlation close to the critical point, and also close to any first order phase transition. Both the experiments and the mean field theory point toward long-ranged correlations near criticality; neither do so for the first order transition. The latter point will require some explaining, to be found below.

2.4 Summary of Landau's mean field theory

As already mentioned, Landau's 1937 result provides a kind of mean field theory which agrees in all essential ways with the results of the main previous workers. The only difference is that it is a specialized theory which is intended to apply mostly to the region near the critical point. From the point of view of the discussion that will follow the main points of the theory are

- **Universality.** The Landau theory gives an equation for the order parameter as a function of the environmental parameters that is universal: It only depends upon the kind of symmetry reflected in the ordering.
- **Symmetry.** A first order phase transition is often, but not always, a reflection of a change in the basic symmetry of the condensed system.

- Interactions. This symmetry change is usually caused by local interactions among the basis constituents of the system.
- Scaling. The results depend upon simple ratios of the environmental parameters raised to powers. For example in the ferromagnetic transition all physical quantities depend upon the ratio t^3/h^2
- Order parameter jump. There is a discontinuous jump in the order parameter at the first order phase transition as in Eq. (1). The jump goes to zero as the critical point is approached, with critical index $\beta = 1/2$.
- heat capacity jump. The heat capacity has a discontinuous jump at the critical point. In particular for $h = 0$ the heat capacity is larger immediately into the ordered region than its value immediately into the disordered region. This behavior is shown in Figure (5).
- Correlation length. The correlation length goes to infinity at criticality as in Eq. (3) with an index $\nu = 1/2$.

As we shall see, the Landau theory has been replaced by a *renormalization group* theory of phase transitions. The qualitative properties of the Landau theory, like universality and scaling, have been retained but all the quantitative properties of the theory, for example, the values of the critical indices, have been replaced.

3 Beyond (or Beside) Mean Field Theory

Mean field theory began to lose favor in the scientific community almost as soon as Landau stated it in its generalized form. This section will describe the process of displacement of mean field theory, at least for behavior near the critical point, which we might say began in 1937 and culminated in Wilson's enunciation of a replacement theory in 1971[27].

Landau's theory provided a standard and a model for theories of general phenomena in condensed matter physics. Looking at Landau's result one might conclude that a theory should be as general and elegant as the phenomena it explained. The mean field theories that arose before (and after) Landau's work were partial and incomplete, in that each referred to a particular type of system. That was certainly necessary in that the details of the phase diagrams were different for different kinds of systems, but somewhat similar for different materials of the same general kind. Landau's magisterial work swept all these difficulties under the rug and for that reason could not apply to the whole phase diagram of any given substance. Thus, if Landau were to be correct he would most like be so in the region near criticality. Certainly his theory is based upon an order parameter expansion that only is plausible in the critical region. However, precisely in this region, as we shall outline below both theoretical and experimental facts were developed that contradicted his theory.

3.1 Experimental facts

I have already mentioned that the ghosts of Andrews and van der Waals might have whispered to Landau that a theory which predicts $\beta = 1/2$ near criticality cannot be correct. However there was also a much larger body of early work which pointed to the conclusion that mean field theory was wrong, at least for fluids. These early data, developed and published by J.E. Verschaffelt[14] and summarized by Levelt Sengers[15], touched almost every aspect of the critical behavior of fluids. Verschaffelt particularly stresses the incompatibility of the data with mean field theory. But these data certainly did not dissuade Landau, who perhaps had never heard of them.

These same experimental facts appear once more in the 1945 work of E.A. Guggenheim,[21] who compiled data on the relation among pressure, density, and temperature for a wide variety of fluids. This relation among these three is called the *equation of state*. He was mostly looking for evidence related to the principle of corresponding states, that is the idea that the equation of state is the same for almost all fluids. He says “The principle of corresponding states may safely be regarded as the most useful by-product of van der Waals’ equation of state. While this [van der Waals] equation of state is recognized to be of little or no value, the principle of corresponding states as correctly applied is extremely useful and remarkably accurate.” He then devotes most of this work to examining the data which might give support to his universality for four noble gases together with oxygen, nitrogen, carbon dioxide, and methane. Specifically he examined data for liquid-vapor coexistence on the line of the liquid-gas phase transition, see Figure (4) and fits the data to a power law with $\beta = 1/3$, rather than the mean field value $\beta = 1/2$. The latter value clearly does not work; the former fits reasonably well. Thus “corresponding states” receives support in this region, but not mean field theory *per se*.

But neither Guggenheim nor Kamerlingh Onnes[15] before him was ready to receive information suggesting that behavior in the critical region was special, so that former rejected mean field theory while the latter accepted it with reservations as to its quantitative accuracy.

Later, data on heat capacities near liquid gas phase transitions became available. (The heat capacity is the derivative of free energy with respect to temperature.) Mean field theory predicts a discontinuity in the constant volume heat capacity as in Figure (5). Among the first experiments in this direction was carried out by Kellers[28], who looked at the normal fluid to superfluid transition in Helium⁴. (See Figure (6).) The data in this phase transition seemed to support the view that the heat capacity diverges weakly, perhaps a a logarithm of $|t|$, as criticality is approached. Similar heat capacity curves were observed by Alexander Voronel’[29, 30] in the liquid gas transition of classical gases, and in further work in Helium[31].

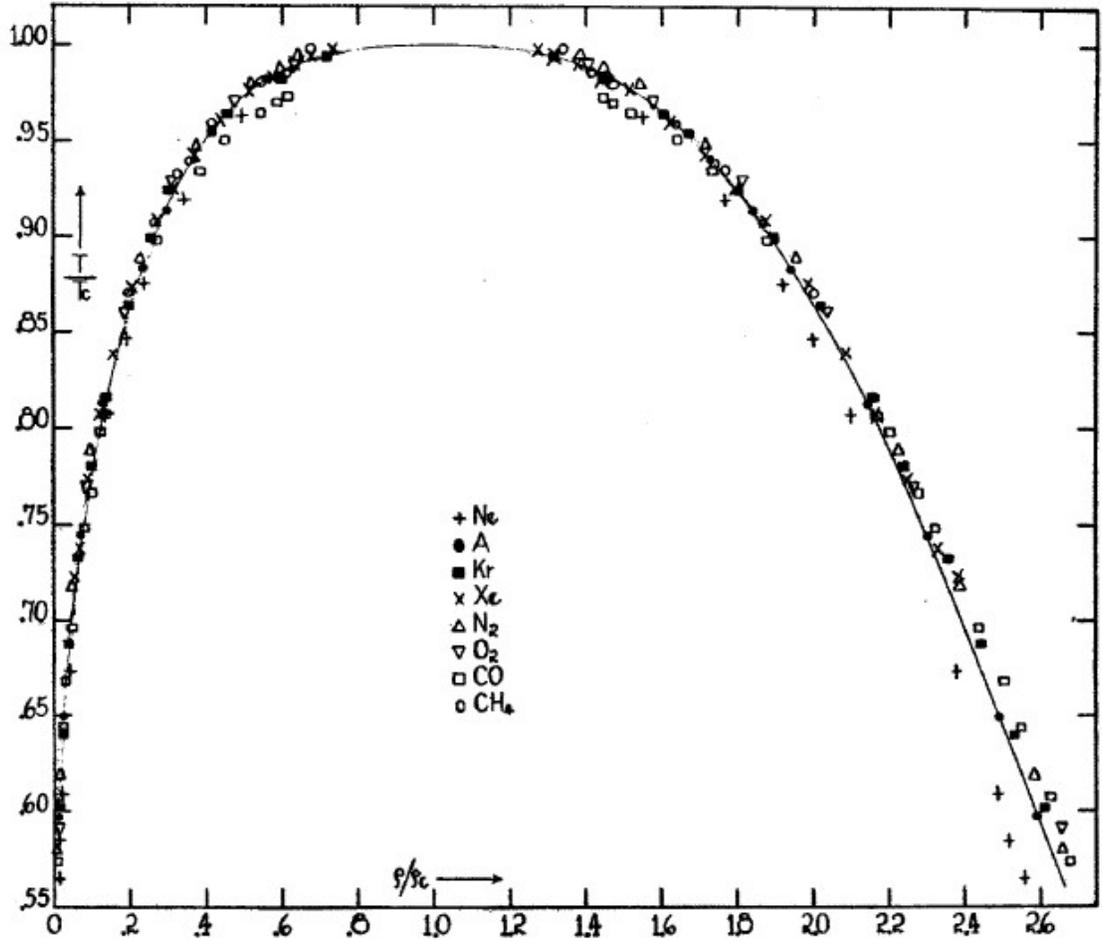


Figure 4: Density jump for several fluids. The data comes from their lines of first order phase transitions. This picture, drawn from Guggenheim[21], plots along the x -axis the density divided by the critical density and on the y -axis the temperature divided by the critical temperature. The symbols give the densities of several fluids in their vapor phase on the left and their liquid phase on the right. The top portion of the curve fits a power law with $\beta = 1/3$.

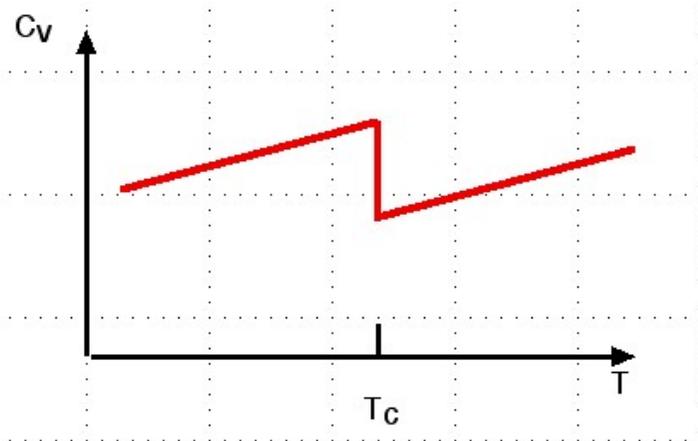


Figure 5: Cartoon sketch of heat capacity in neighborhood of critical temperature as predicted by mean field theory. The heat capacity is higher below T_c because there is an additional temperature dependence in the energy in this region produced by a term proportional to the square of the order parameter.

3.2 Theoretical facts

As we have seen, experimental evidence suggested that mean field theory was incorrect in the critical region. A further strong argument in this direction came from Lars Onsager's exact solution[32] of the two dimensional Ising model, followed by C.N. Yang's calculation[33] of the zero-field magnetization for that model. Onsager's logarithmic result for the heat capacity diverged as did the experimental observations, as shown for example in Figure (6), but did not resemble the discontinuity of mean field theory.⁵

Yang's results, for which $\beta = 1/8$, also disagreed with mean field theory, which has $\beta = 1/2$. Yang's index-value also differs substantially from the experimental results observed in three-dimensional systems, which has β roughly equal to $1/3$, but they offered neither support nor comfort to mean field theory. The Onsager solution implies a correlation length with $\nu = 1$, see Eq. (3), which is not the mean field value $\nu = 1/2$.

The most systematic theoretical discrediting of mean field theory came from the series expansion work of the King's College (London) school, under the leadership of Cyril Domb, Martin Sykes, and after a time Michael Fisher. Much of the story of this group's activities can be found in the books by Domb[34] and a study of the history of the Ising model by Martin Niss[4]. Recall that the

⁵Onsager's results looked different from those depicted in Figure (6) in that they showed much more symmetry between the high temperature region and the low temperature region. This difference reflects the fact that two dimensional critical phenomena are markedly different in detail from three dimensional critical phenomena. Further, subsequent work has indicated that none of the heat capacity singularities shown in Figure (6) are actually logarithmic in character. They are all power law singularities.

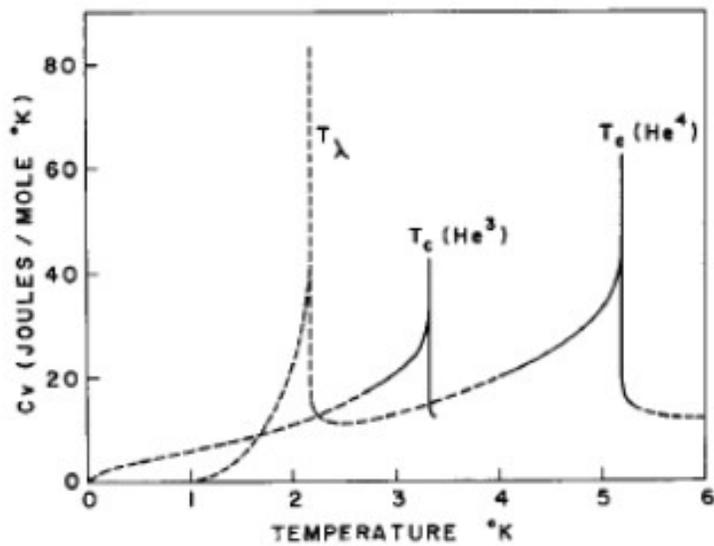


Figure 6: Heat capacity as measured. This picture, drawn from the work of Moldover and Little[31] shows measured heat capacities for the normal-superfluid transition of Helium⁴, labeled as T_λ , and the liquid-vapor transition of Helium³ and Helium⁴. Note that all three heat capacities seem to go to infinity, in contrast to the prediction of mean field theory. These data certainly draw ones attention to the critical region.

Ising model is a simplified model which can be used to describe magnetic transitions. It is described by a strength of the coupling between neighboring spins proportional to a coupling constant J . The statistical mechanics of the model is defined by the ratio of coupling to temperature, specifically $K = -J/(kT)$, where k is the Boltzmann constant, used to translate temperatures into energy units. One can get considerable information about the behavior of these models by doing expansions of quantities like the magnetization and the heat capacity in power series in K , for high temperatures, and e^{-K} , for low temperatures. The group at King's developed and used methods for doing such expansions and then analyzing them to obtain approximate values of critical indices like β and ν . The resulting index-values in two dimensions agreed very well with values derived from the Onsager solution. In three dimensions, models on different lattices gave index values, roughly agreeing with experiment on liquids and magnetic materials, but differing substantially from predictions of mean field theory. This work provided a powerful argument indicating that mean field theory was wrong, at least near the critical point. It also played a very important role in focusing attention upon that region.

One reason for doubting mean field theory, ironically enough, came from Landau himself. In 1941, Kolmogorov[35] developed a theory of turbulence based upon concepts similar to the ones used in mean field theory, in particular the idea of a typical velocity scale for velocity differences over a distance r . These differences would, in this theory, have a characteristic size which would be a power of r . Landau criticized this theory saying that it did not take into account fluctuations[36], whereupon Kolmogorov modified the theory to make it substantially less similar to mean field theory[37].

3.3 Spatial structures

The spatial structure of mean field theory does not agree with the theorem that phase transitions can only occur in infinite systems. Mean field theory is based on the alignment of order parameter values at neighboring sites, so that particles will order if neighboring particles are ordered also. Any collection of couplings in which the bonds can form a closed loop can have a mean field theory phase transition. Thus, four particles forming a square with four interactions connecting the corners of the square are quite sufficient to produce a phase transition in mean field theory. On the other hand, the extended singularity theorem insists that the occurrence of a phase transition requires some sort of infinity, most often the existence of an infinite number of interacting parts within the system. Thus mean field theory is inconsistent with statistical mechanics⁶. According to George E. Uhlenbeck [38], Hendrick A. Kramers was the first to point out that the sharp singularity of a phase transition could only occur in a system with some infinity built in. Apparently the point remained contentious as late as 1937. I quote E. G. D. Cohen's description of material contained in

⁶Arthur Wightman[40] has emphasized that Gibbs could certainly have known that phase transition are properties of infinite systems. However, Gibbs' book on statistical mechanics[9] never did anything quite as specific as discuss phase transitions.

another work of Uhlenbeck[39]: “Apparently the audience at this Van der Waals memorial meeting in 1937, could not agree on the above question, whether the partition function could or could not explain a sharp phase transition. So the chairman of the session, Kramers, put it to a vote.” The result was a 50-50 split.

So some attention was given to this point. However, Landau himself had information which would argue that mean field theory was a weak basis for a theory of phase transitions. The general point has to do with systems which are infinite in only one of their dimensions. After the formulation of the Ising model, Ising himself solved the model in one dimension. He found no phase transition[4] in this situation. Some scholars thought that the model itself was not rich enough to give a phase transition. However, Landau[41] showed that in any system which was infinite in only one of its dimensions fluctuations would effectively separate itself into noncommunicating finite pieces and these pieces would show no phase transition. This argument was perfectly general and correct. Mean field theory gave phase transitions in one dimension. Thus something must be wrong with mean field theory.

As we shall see, what is wrong with mean field theory is that in the critical region the average behavior of the average order parameter can be completely swamped by fluctuations in this quantity. In 1959 and 1960, A. P. Levanyuk[42] and V.L. Ginzburg[43] described a criterion which one could use to determine whether the behavior was dominated by average values or by fluctuations. For example, when applied to critical behavior of the type seen in the simplest version of the Ising model, this criterion indicates that fluctuations dominate in the critical region whenever the dimension is less than or equal to four Hence mean field theory is wrong[46] for all the usual critical phenomena in systems with dimension smaller than or equal to four⁷. Conversely, this criterion suggests that mean field theory is the leading behavior above four dimensions.

4 New foci; new ideas

4.1 Bureau of Standards conference

So far, the field of phase transition had lived up perfectly to Thomas Kuhn’s[47] view of the conservatism of science. Before World War II there was no theory of phase transitions save mean field theory. There was no theory or model that yielded Eq. (1) with any value of β different from one half, so there was no focus for anyone’s discontent. For this reason, the mean-field-theory point of view continued on, despite evidence to the contrary, until a set of events occurred which would move the field in a new direction. One crucial event was the conference on critical phenomena held at the U.S. National Bureau of Standards

⁷There are exceptions. Mean field theory works quite well for the usual superconducting materials studied up through the 1980s[44]. However, mean field theory does not work for the newer “high-temperature superconductors”, a class discovered in 1986 by Karl Müller and Johannes Bednorz[45].

in 1965[48]. The point of this conference was that behavior near the critical point formed a separate body of science which might be studied on its own merits, independent of the rest of the phase diagram. In the years just before the conference, enough work[49, 50, 51] had been done so that the conference could serve as an inauguration of a new field. We have mentioned the experimental studies of Kellers and of Voronel's group. At roughly the same time important theoretical work was done by Pataskinskii and Pokrovsky[52], Benjamin Widom[55] and myself[56], which would form a basis for a new synthesis. The experimental and theoretical situation just after the meeting was summarized in reviews[46, 51, 50]. This section begins by reporting on those new ideas and then describes the culmination of these ideas in the work of Kenneth G. Wilson[27].

4.2 correlation function calculations

For many years the Landau group had been working on putting together a field theoretical basis for critical point work. Two young theoreticians, A. Z. Pataskinskii and V. L. Pokrovsky, focused their attention upon the correlated fluctuations of order parameters at many different points in space. They succeeded[52] in getting the right general structure of the correlations, but they got a wrong value of a critical indices. Nonetheless they pointed the way toward future field theoretic calculations of correlation behavior.

In parallel, I calculated[53] the long-distance form of the spin correlation function for the two-dimensional Ising model by making use of the Onsager solution. This was the part of a long series of calculations which would give insight into the structure of that model[54].

Benjamin Widom[55] (See Figure (7).) reported at the National Bureau of Standard meeting upon a phenomenological theory in which he used insight and previous results to obtain a formula for the scaling structure of the main thermodynamic derivatives of near-critical fluids. He also got a scaling relation for the surface tension, the free energy of the boundary between liquid and vapor. In this remarkable work, he correctly pointed out the scaling structure of the future theory.

4.3 Block transforms

Widom supplied much of the answer to questions about the thermodynamics of the critical point. I then supplied a part of the strategy for deriving the answer[56]. I will now describe the method in a bit of detail since the calculation provides some insight into the structure of the solution.

Imagine calculating the free energy of an Ising model near its critical temperature based upon the Ising model interactions incorporated in Ising's Hamiltonian function for the problem. The result will depend upon the number of lattice sites, the temperature deviation from criticality and the dimensionless magnetic field. Next imagine redoing the calculation using a new set of variables constructed by splitting the system into cells containing several spins and



Figure 7: Michael Fisher, foreground, and Benjamin Widom, background, at a 65th birthday party for Michael.

then using new spin variables. Each of the new spin variables are intended to summarize the situation in a block containing several old spin variable. (See Figure (8)) To make that happen one can, for example, pick the new variables to have the same direction as the sum of the old spin variables in the block and the same magnitude as each of the old variables. One can then do an approximate calculation and set up a new “effective” free energy calculation which will give the same answer as the old calculation based upon an approximate “effective” Hamiltonian making use of the new variables. . One argues on the basis of universality that the new Hamiltonian can have the same structure as the old one but that the new parameters in it, the number of lattice sites, the temperature deviation from criticality, and the dimensionless magnetic field all are proportional to the corresponding old parameters. This proportionality is a representation of scaling, and the coefficients in the linear relations define the scaling relations among the variables. These scaling relations then give a theory with all the empirical relations given by Widom[55], but backed by the outlines of a conceptual and calculational scheme.

Note that here scaling is viewed as a change in the effective values of the thermodynamic parameter produced by a change in the length scale at which the system is analyzed. The length scale must be irrelevant to the determination of the eventual answer and must drop out of the final result for the free energy. It is this dropping out that gives the empirical relations proposed by Widom.

This theoretical work of references [52, 70, 71, 55, 56] was all well-received. The review paper of [46] was particularly aimed at seeing whether the new phenomenology agreed with the experimental data. It reviewed most of the recent

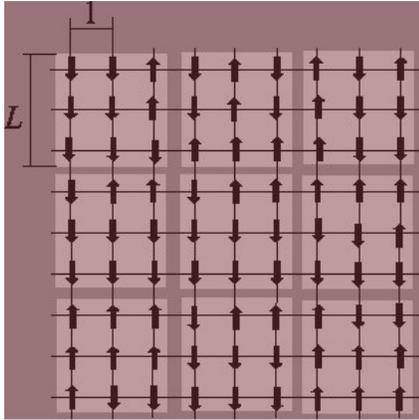


Figure 8: Making blocks. In this illustration a two dimensional Ising model containing 81 spins is broken into blocks, each containing 9 spins. Each one of those blocks is assigned a new spin with a direction set by the average of the old ones, We imagine the model is reanalyzed in terms of the new spin variables.

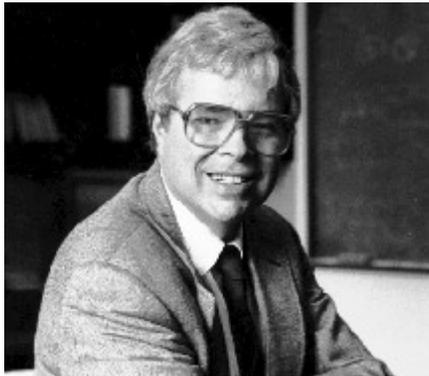


Figure 9: Kenneth G. Wilson. His graduate studies were carried out at the California Institute of Technology. He spent two years in the Kellogg Laboratory of nuclear physics, and then worked on a thesis for Murray Gell-Mann. This was followed by a Junior Fellowship at Harvard, a year's stay at CERN, and then an academic appointment at Cornell. The renormalization group work was done while Wilson was at Cornell.

experiments but missed large numbers of the older ones which are included in references[15, 34]. All of this activity validated the consideration of the critical region as an appropriate subject of study and led to a spate of experimental and numerical work, but hardly any further theoretical accomplishments until the work of Wilson[27].

4.4 The Wilson Revolution

Around 1970, these concepts were extended and combined with previous ideas from particle physics[58, 59] to produce a complete and beautiful theory of critical point behavior, the renormalization group theory of Kenneth G. Wilson[27]. (See Figure (9).) The basic idea of reducing the number of degrees of freedom, described in reference[56], was extended and completed.

Wilson, in essence, converted a phenomenology into a calculational method by introducing ideas not present in the earlier phenomenological treatment[56]:

- Instead of using a few numbers to describe environmental parameters, e.g.

t, h , he extended the list of possible parameters to include all the kinds of coupling terms which might be found in the Hamiltonian of the system. Then the statement that a renormalization produced exactly the same kinds of couplings, while changing the parameters which described these couplings is reduced to a tautology.

- Wilson considers indefinitely repeated transformations, as in the earlier particle physics work. Each transformation increases the size of the length scale. In concept, then, the transformation would eventually reach out for information about the parts of the system which are infinitely far away. In this way, the infinite spatial extent of the system became part of the calculation. The idea that behaviors at the far reaches of the system would determine the thermodynamic singularities were thence included in the calculation.
- Furthermore, Wilson added the new idea that a phase transition would occur when the transformations brought the coupling to a *fixed point*. That is, after repeated transformations, the couplings all would settle down to a behavior in which further renormalization transformation would leave them unchanged.
- Finally, at the fixed point, the correlation length would be required to be unchanged by renormalization transformations. The transformation multiplies the length scale by a factor that depends upon the details of the transformation. Wilson noted that there are two ways that the correlation length might be unchanged. For transformations related to a continuous transition, the correlation length is infinite, thence reflecting the infinite-range correlation. For transformations related to first order transitions, the correlation length is zero reflecting the local interactions driving the transition.

A very important corollary to the use of repeated transforms is the idea of *running coupling constants*. As the length scale changes, so do the values of the different parameters describing the system. In the earlier field theoretical work[58, 59], the important parameters were the charge, masses, and couplings of the “elementary” particles described by the theory. The change in length scale then changed these from the “bare” values appearing in the basic Hamiltonian for the problem to renormalized values which might be observed by experiments examining a larger scale.. The use of renormalized or “effective” couplings was current not only in particle theory, but also in quasiparticle theories which are pervasive in condensed matter physics[60]. In these theories one deals with particles that interact strongly with one another. Nonetheless, one treats them using the same Hamiltonian formalism that one would use for non-interacting particles. The only difference from free particles is that the Hamiltonian is allowed to have a position and momentum dependence that reflects the changes produced by the interactions.

4.5 New concepts

The renormalization revolution and the phenomenological work which preceded it included several very important new concepts which were applied not only to critical phenomena but also to many other situations. These new ideas include, in addition to the running couplings described above,

- Fluctuations. The behavior at the critical point is determined by fluctuations in all kinds of physical quantities, with the order parameter being the most important.
- Scaling. Near criticality, fluctuations occur over a very wide range of length scales. The near-critical couplings like t and h can each be measured against powers of the relevant length scale.
- Universality classes. The universality idea was used to classify all the different possible behaviors at critical points. There are only a limited number of different universality classes. When different phase transition fall into the same class, all aspects of their critical behavior then turn out to be identical. For example, the liquid-gas phase transition and the Ising model are in the same universality class.
- Symmetry. Different symmetries and different numbers of dimensions imply different universality classes. Thus a superfluid transition on a surface is quite different from one in bulk.

5 Building upon the revolution

5.1 applications to critical phenomena

This Wilson renormalization theory provided a basis for the development of new methods that could be used for building an understanding of critical phenomena. One example is the ϵ expansion of Wilson and Fisher[57]. This calculational method focuses upon the dependence of physical quantities upon dimension, by uses renormalization transforms near four dimensions, where mean field theory is almost, but not quite, correct. The idea of using the dimension of the system as an variable parameter seems a bit strange at first sight. However, the method gave quite accurate results for of critical behavior for many different models in three dimensions. These results helped convince people that both the variable-dimension method and the renormalization method were valid. Many different results were constructed using variable-dimensions.

Another method, *real space renormalization* was pioneered as a calculational technique by Niemeijer and van Leeuwen[61]. This method is better suited than the epsilon expansion for calculations in lower dimensions. The method is extensively described in reference [62].

Following the work of Wilson, a tremendous amount of theoretical work was done in a very short period. It soon seemed that all of critical phenomena had been explained.

5.2 particle physics

The renormalization group was closely allied to developments in particle physics. It had grown out of work aimed at taming the infinities in particle applications of field theory. In fact, the applications in the two disciplines were very closely parallel. In both cases, one visualized a basic theory formulated at scale much smaller than the human scale of observations. In both cases, the idea was to interpolate between the effects at the two scales by using the running coupling constants. In condensed matter physics, one imagined that the experimentalist “dialed” experimental parameters so as to bring the system close to criticality. This choice of parameters would make the coherence length rather long so that the effect of critical fluctuations would be observable. In particle physics, the analog of the coherence length was the mass of an observable particle. Or rather the mass was the analog of one over the coherence length, when appropriate factors of Planck’s constant and the speed of light were factored in. If that mass were directly set at the very small scales of the fundamental theory, it would be unobservably large. Experimentally observable masses are somehow reduced by some approximate symmetry principle, and perhaps by some imperfectly understood process of “dialing” coupling constant. Then the observed masses are modified by the “running” process. So the calculations in particle physics’ field theory are in many ways similar to those in statistical physics’ critical phenomena[63].

5.2.1 asymptotic freedom

One set of very important field theories were the SU2 and SU3 gauge theories which undergird the standard model of particle physics. David Gross and Frank Wilczek[64] and in parallel David Politzer[65] discovered that renormalization made these interactions stronger at larger distances. Correspondingly, they would be very weak at shorter distances, which would bring in higher energies. his result permitted calculations of high energy standard model effects by expansions in the weakened couplings and thereby brought effects at modern accelerators within the realm of accurate calculation.

5.2.2 conformal field theory

Field theory itself gained considerable in depth after the renormalization revolution. One of the major advances was the development of conformal field theory by A.A. Belavin, A.M. Polyakov, and A.B. Zamolodchikov[66, 67]. This is a version of field theory that applies especially to situations in which the coherence length is infinite. Of course, that is specifically the case which holds in continuous phase transitions. The specialization to conformal situations gives particularly powerful results in two dimensions. In that case, one can pick out a large group of familiar models, including the Ising model, which can be mostly solved by using conformal field theory[68].

5.3 Singularities in first order transitions

In a brilliant pair of papers[69], T.D. Lee and Yang developed a description of how singularities actually appear in phase transitions. By extending the definition of the Ising model's magnetic field to include complex values, they found singularities in the free energy of the Ising model. Most of these singularities were off into the complex plane and did not cause any physical singularities. However, they showed that, for temperatures at or below the critical temperature, these singularities approached the line of real magnetic field values. This pinching produced singularities in the free energy. However, this Lee-Yang calculation was a beginning, not an end. It located the singularities in the complex plane but still did not define their exact nature. Since the Onsager solution only gave values of the free energy for zero magnetic field, it too could not be helpful in establishing the nature of these singularities.

As we have discussed in detail, renormalization group calculations defined the nature of the singularities at the critical point, but they did not much touch upon the singularities which were expected to occur on the zero field line below the critical temperature.

One might guess that the only singular behavior on this line was the discontinuous jump in magnetization. This guess would accord with the folk wisdom which said that first order transitions were a sort of accident that occurred whenever the difference between the free energies of two different phases happened to be zero. The next step was to say that this accidental equality would leave no mark on the free energy itself. However, that last statement turns out to be wrong. Even before the nature of the singularities at the critical point were established, Fisher[70] (See Figure (7).) and A. F. Andreev[71] imagined a system near a first order phase transition as a set of regions of the two different phases in contact with each other. They then estimated the effect of these fluctuating "droplets" upon the free energy and thereby upon the entire statistical behavior of the system. In this way, they developed calculations of the kinds of singularities which could occur at first order phase transitions. These works remain as the best description of singularities in this domain. Fisher's work also pointed the way toward scaling theories of continuous transitions, but the scaling relations were not exactly the same as the ones which finally emerged.

These singularities in first order transitions are a result of theory, but are almost invisible, both to experiment and to simulation. In fact, they are invisible to theory as well at least if the theory is limited to magnetic field equal to zero. All corrections from droplet singularities seem to pop up as very small terms which appear at small values of magnetic field. Further the largest fluctuating droplets are very rare, and take a long time to develop. These properties makes them very hard to observe.

5.4 Other singularities

5.4.1 Lee Yang singularities

The exact nature of the Lee Yang singularities[69] as they arise in the complex plane for temperatures above the critical temperature was established by Fisher[72] and others. The result was that these singularities could be analyzed as the usual kind of phase transition, but displaced into the complex plane. In two dimensions, detailed exact information about the singular behavior was available through the use of conformal field theory.

5.4.2 Bose-Einstein transition

For interacting particles, as in Helium⁴ the transition to superfluid flow is a standard phase transition problem in the same universality class as an XY magnetic phase transition. However, there is an analogous transition in the non-interacting case. It was originally considered by Satyendra Nath Bose[73] and Einstein[74]. It is treated in beginning statistical mechanics courses as an example of the use of the grand canonical ensemble, a method of averaging originally introduced by Gibbs in his book on statistical mechanics[9]. In this case, there is a singularity at the phase transition to the Bose condensed state in which a finite fraction of the particles in the system are described by a single wave function. The singularity here is caused by the ensemble's possible inclusion of an infinite number of particles. This inclusion is possible precisely because the particles do not interact so it is possible for an infinite number of them to appear in a finite volume. In this case, the fluctuations play a substantial role in the analysis, but the mean field behavior is dominant.

5.4.3 glasses

Despite the familiarity of window glass, glass is a very special state of matter. Glasses are produced in situations in which the particles in the glass get stuck in one of many different regions in “configuration space” and only explore that relatively small region, at least in any reasonable period of time. Over longer times, the size of the region will grow very slowly, but the region never encompasses most of the possible configurations. The repeated exploration of a slowly growing region of configurations is characteristic of a behavior described as “glassy”. Such glasses tend to occur in many materials with relatively strong interactions. They are believed to be in some cases a dynamical property of materials[75], and in others an equilibrium property described by an extension of Gibbsian statistical mechanics. Present-day condensed matter science does not understand glassy behavior. Some people believe that glasses can undergo a phase transition. But as people have looked for some infinitely extended correlation, nothing like this has been found. The relation between glasses and the “extended singularity theorem” remains obscure.

5.4.4 jamming

Particles in glasses are in motion. In another related phenomenon, the jamming transition, the particles are stuck[76] and are not moving at all. The usually quoted example of this is the pouring of dry cereal through an aperture. For a reasonably small aperture, the cereal may pour for a while and then get stuck because each grain is jammed up against the next one. This jamming is a kind of phase transition which, in recent years, has become a subject of scientific study.

Like the glass transition, the jamming transition is not fully understood. The jamming might involve a singularity produced by the potentially infinite forces produced when one grain squeezes against the next. That is one kind of infinity. It is likely to further involve an infinite spatial extension in which a whole chain of grains pushed against one another produces a chain of forcing that can extend over a potentially infinite distance. Several different diverging length scales have been proposed[77] to explain the situation in which the system is nearly jammed.

5.4.5 quantum phase transitions

Everything in nature obeys the laws of quantum mechanics. In that sense, all phase transitions are quantum in their nature. However many phase transitions like the liquid-gas transition can be rather completely understood by using the concepts of classical physics. We describe them by saying that information about the value of some order parameter is passed from place to place within the system. The extended singularity theorem tell us that for most phase transitions, this information is, remarkably enough, transferred over the entire system, a potentially infinite distance.

In classical mechanics all information is in the form of numbers. This information describing a classical phase may be a vectors or even a tensor, but that is as complex as it usually gets. But in quantum theory, information may be much richer in character. It may describe the entanglement of data about two subsystems. The usual example of the two systems might be a spin variable described by its wave function, and the state (alive or dead) of Professor Schrödinger's cat, described in terms of its own wave function. This entangled information might perhaps be transferred by some phase of a quantum nature over an entire material.

We know that there are quantum phase transitions. For example, the behavior of the materials known a high temperature superconductors[45, 78] probably involve one or more kinds of quantum phase transitions. And we would like to learn what kinds of information are implicated in such transitions.

Physics is candy for the intellect!

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