

Chapter 1.1

An Overview

What are cooperative phenomena? In physics, cooperative phenomena mean global changes in the structure and physical properties of a system that takes place cooperatively when some external variable, in most cases temperature, is changed continuously in a certain interval. Consider a solid for instance. By warming it up moderately one expects to observe a small dilatation of its overall dimensions, which is reflected at the microscopic level by small increases, of the order of one part in 10,000 or less, per degree Kelvin in the unit cell parameters. The same can be said of the specific heat. If the ambient temperature of the solid is low in comparison with its characteristic Debye temperature, the specific heat will increase smoothly according to Debye's T^3 law. If the ambient temperature is above the Debye temperature, one may expect a small increase with T due to anharmonic contributions, which are, in general, small. But ordinarily we do not expect a drastic change in any physical property of the solid if the increase in temperature is small. This is precisely what happens when a cooperative phenomenon in the system takes place: some physical properties, specific heat, lattice parameters, etc., manifest pronounced changes, continuous or discontinuous, as the system approaches the phase transition point. Very often the system goes from a lower temperature ordered phase to a higher temperature disordered phase, and the phase change takes place in such a way that as the disorder increases it becomes easier to increase further the disorder in the system. That is why the term "cooperative phenomena" is in order.

This is, of course, familiar to any student of condensed matter physics. What is perhaps not so familiar is the high degree of underlying similarity among apparently very different kinds of phase transition, such as

Table 1.1.1. Cooperative phenomena.

Transition	Conjugated variables	Discovery	First successful theory
Liquid/vapour	$P - V$	T. Andrews, 1872	J. van der Waals, 1874
Ferromagnetic/ paramagnetic	$H - M$	P. Curie, 1895	P. Weiss, 1907
Superconductor/normal	$() - N$	K. Onnes, 1906	J. Bardeen, L. Cooper, J. Schrieffer, 1957
Order/disorder (alloys)	$() - \zeta$	G. Tamman, 1919	W. Bragg, E. Williams, 1934
Ferroelectric/paraelectric	$E - P$	J. Valasek, 1921	W. Mason, 1947
Superfluid/normal	$() - N$	W. Keesom, A. Keesom, 1935	N. Bogoliubov, 1946
Ferroelastic/paraelastic	$X - x$	—	K. Aizu, 1969

Conjugated variables: P = pressure, V = volume, H = magnetic field, M = magnetization, N = number of bound Cooper pairs per unit volume in a superconductor, $\zeta = (R - W)/(R + W)$, R = number of rightly located atoms, W = number of wrongly located atoms in an order-disorder alloy, E = electric field, P = polarization, X = stress, x = strain, N = number of (Bose) condensed atoms in a superfluid.

the liquid-vapor transition, the ferromagnetic transition, and the order-disorder transition in alloys, to name a few. Table 1.1.1 gives a more comprehensive list of phase transitions (cooperative phenomena) in a number of systems, making explicit the pair of conjugated variables involved (whose product is either an energy or a dimensionless number if the magnitudes of the variables are normalized), the year of discovery of the first quantitative characterization, and the year of publication of the first simple theory for the cooperative phenomenon in question.

While the first successful theories quoted in the last column of Table 1.1.1 are not exactly equivalent, all of them have much in common. The theory of P. Weiss for the ferromagnetic/paramagnetic transition can be taken as a prototype because of its extreme simplicity. We will see in subsequent sections that the effective field concept can be used as the basis to reformulate in very simple terms the theories of most cooperative phenomena listed in the table.

There are many excellent monographs dealing with the modern theories of phase transitions and critical phenomena.¹⁻⁴ The ground covered by the literature on this subject is very broad. Our purpose (a modest one) is to introduce the reader to the effective field theories of phase transitions, and we do not need to enter into the many important subtleties of these modern theories. A few introductory remarks are probably in order, however,

concerning some of the basic features of phase transitions:

(i) *Symmetry breaking.* A phase transition is usually accompanied by a breakdown of symmetry. For instance, a ferromagnet at a temperature above its transition temperature ($T_c =$ Curie temperature) has zero magnetization in zero field; it is symmetric, i.e., does not have any preferred direction with respect to the magnetization. As we lower T below T_c , however, a spontaneous magnetization develops in a specific direction. The forward and backward directions along the line of magnetization become inequivalent and, consequently, the earlier symmetry breaks down. Some ferromagnets are multiaxial, and lowering T below T_c may break down the crystal in several domains with magnetizations along mutually perpendicular axes. Others are uniaxial and they can break only into domains pointing in one direction or in the opposite direction (180° apart). But in both cases it suffices to apply a very small magnetic field along one preferred direction during the slow cooling process to get a single-domain crystal. It may be noted, on the other hand, that not all phase transitions are accompanied by symmetry breaking: for instance, in a liquid–vapor transition the system remains isotropic below the transition temperature, only its density (volume) changes drastically.

(ii) *Continuity or discontinuity.* The phase transition can take place either in a continuous fashion (usually these transitions are called second order transitions) or in a discontinuous fashion (first order transitions). For instance, in ferroelectric systems, in which the order parameter is the electric polarization, going from $T < T_c$ to $T > T_c$, the polarization can go to zero continuously or discontinuously. In some cases it is possible to use a variable external force (a uniaxial stress to the crystal along a given direction) to change the nature of the transition from first order to second order. If we can change the variable external force in arbitrarily small steps we go from first order to second order passing through a threshold point between the two cases, which is called a “tricritical point.”

(iii) *Dimensionality and universality classes.* A physical system can be thought of as being made up of chains of atoms (or groups of atoms) which when they are close together in a single plane make up a surface, and many surfaces together parallel to each other form a three-dimensional lattice. For instance, in a ferromagnetic crystal the relevant units are the atomic spins of certain atoms periodically arranged in space. If the arrangement of the spins is such that they form parallel chains widely separated from each other, the dimensionality of the system is said to be one. If the arrangement of the

spins in parallel sheets widely separated from the next sheets the dimensionality is three. But, in addition, we have to consider the dimensionality of the ferromagnetic units themselves, the atomic spins, which are responsible for the development of a non-zero order parameter (the magnetization) at $T < T_c$. In some systems, the combined cooperative interaction and local crystal field interaction force the spins to point up or down in a specific direction, which implies an order parameter dimensionality one (Ising case). In other cases, moving from one spin to the next involves a rotation within a single plane, which repeats itself going to the following next spin and so on, implying an order parameter dimensionality two (X - Y case). Still in other ferromagnetic systems the allowed direction for the spins is not restricted to a line or to a plane but may be in any spatial direction, i.e., they have order parameter dimensionality three (Heisenberg case). It has been one of the great theoretical discoveries of the late 1960s and early 1970s to establish that the critical behavior at a phase transition (i.e., the behavior of the order parameter and its associated susceptibilities very close to the transition temperature, where fluctuations play a major role) is entirely determined by the dimensionality of the system together with the dimensionality of the order parameter. There would be, therefore, nine physically realizable universality classes, if all 3×3 combinations would involve a phase transition at $T > 0$ K. This, however, is not the case, e.g., the one-dimensional Ising case does not have a phase transition at $T > 0$ K.

(iv) *Anomalies in physical properties near T_c .* The three main variables involved in a phase transition are the order parameter (for instance, in a ferroelectric, the polarization), the conjugated field (e.g., the electric field), and the temperature. (It is possible also to substitute the temperature for another variable, for instance, a pressure sufficient to trigger the transition, in the case of a ferroelectric, keeping the temperature fixed, but this case is less general.) However, the fact that a phase transition takes place makes itself patent very often in anomalies of many other physical properties of the system. In a typical second order ferroelectric transition, the polarization decreases at first very smoothly from its saturation value at $T \cong 0$ K, then the decrease begins to be more pronounced as T_c is approached, and finally it goes down very steeply to zero as $T \rightarrow T_c$. The associated susceptibility (dielectric constant) diverges as T_c is approached from both sides. Measured values of $\epsilon(T_c) = (4dP/dE)_{T_c}$ up to 10^6 have been reported in some ferroelectric systems. The entropy presents also a marked temperature dependence, and the excess specific heat associated with it presents, likewise, a characteristic peak at $T \cong T_c$. The unit cell lattice parameters show

anomalous behavior with temperature near T_c , and so do the corresponding thermal expansion coefficients. For instance, in some uniaxial cases the thermal expansion in the direction of the ferroelectric axis decreases with T at $T \geq T_c$, while the thermal expansion in directions perpendicular to this axis increase with T . The elastic constants $C_{ij}(T)$ also show anomalies, detected by ultrasonic or Brillouin scattering measurements, near T_c . The refractive indices, birefringence, and optical activity are also connected to the order parameter (polarization) and they show anomalous behavior near T_c . Finally, even transport coefficients such as thermal and electric conductivities often present pronounced anomalies in the vicinity of the phase transition.

(v) *Law of corresponding states.* A very interesting feature of many phase transitions is that, using normalized variables, i.e., a dimensionless order parameter (dividing by its saturation value) and a dimensionless temperature (dividing by the transition temperature), one can fit in a single curve sets of data for many different systems undergoing the same type of phase transition. It is said that the collection of systems fulfills a "law of corresponding states," even if the absolute values of order parameter and transition temperature of individual systems differ widely. This is shown in Fig. 1.1.1 for a collection of liquid-vapor phase transitions, as illustrated by E.A. Guggenheim⁵ in 1945, and in Fig. 1.1.1 for the three metallic ferromagnets⁶ Fe, Ni, and Co. In the first case, the order parameter is the

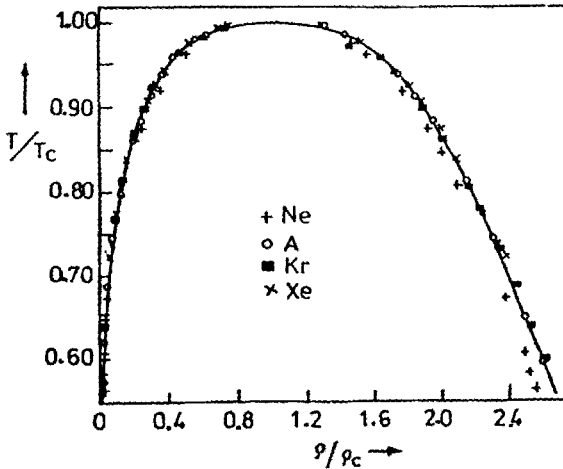


Fig. 1.1.1. Law of corresponding states for liquid-vapor systems.

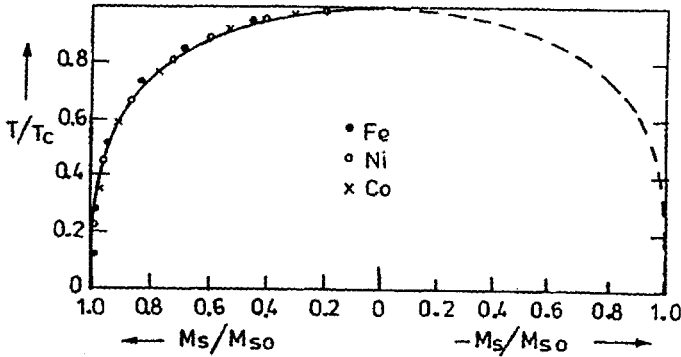


Fig. 1.1.2. Law of corresponding states for ferromagnetic systems.

normalized density of the system. In the second case, the order parameter is the normalized spontaneous magnetization, which can point out in either of two opposite directions. In Fig. 1.1.2, one gets something that resembles Fig. 1.1.1 but is much more symmetric. This reflects the fact that, from the physical point of view, positive and negative magnetizations are equivalent with respect to their zero mean value, while the vapor and liquid state densities are not so symmetrically equivalent with respect to its non-zero mean value.

(vi) *Similarities and differences.* It must be emphasized, therefore, that all types of phase transitions show striking similarities, but they show also characteristic differences among each other. For instance, from a formal point of view, ferroelectric and ferromagnetic transitions are much closer to each other than either of them is to the liquid-vapor phase transition, for instance. This is illustrated in Fig. 1.1.3, where the phase diagram for a liquid-vapor transition (H_2O) is compared with the diagrams for a ferromagnet (Fe) and a ferroelectric (TGS).

(vii) *Direct and indirect approaches.* Phase transitions take place in macroscopic, N -body systems made up of a very large number of atoms or molecules (typically $N = 10^{22}$). A direct solution using the general methods of statistical mechanics (together with considerable mathematical skills) is sometimes possible. An example is Onsager's solution of the two-dimensional Ising model for zero magnetic field, but this is far from the general situation. Another approach is to seek indirect approximate solutions, exploiting existing or realistically assumed symmetries of the system, which result in drastic simplification of the problem at hand. The effective

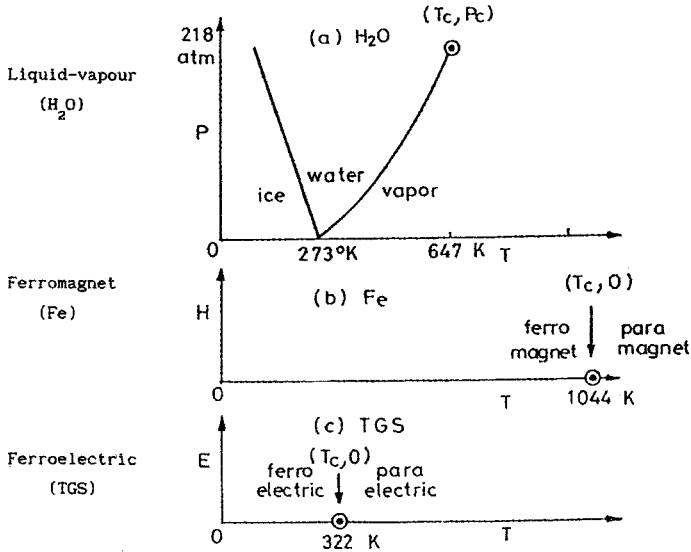


Fig. 1.1.3. Phase diagrams for liquid-vapor, ferromagnetic, and ferroelectric transitions.

Table 1.1.2. Critical exponents.

Definition	Ferromagnet (Ni)	Ferroelectric (TGS)	Effective field model
$m \propto (T_c - T)^\beta, h = 0$	$\beta = 0.33$	$\beta = 0.50$	$\beta = 1/2$
$m \propto h^{1/\delta}, T = T_c$	$\delta = 4.2$	$\delta = 3.0$	$\delta = 3$
$\chi \equiv (\partial m / \partial h) \propto (T - T_c)^{-\gamma}_{T, h \rightarrow 0}$	$\gamma = 1.32$	$\gamma = 1.0$	$\gamma = 1$
$C \propto (T - T_c)^{-\alpha}, h = 0$	$\alpha = -0.10$	$\alpha \approx 0$	$\alpha = 0$

m = order parameter, T_c = transition temperature, h = field conjugated to order parameter (H, E), χ = susceptibility, C = specific heat.

field approach, which assumes complete homogeneity throughout the system, or, at least, throughout any single domain in it, is a case in point. It is often convenient to start with the indirect, simplified approach, and then proceed to the direct approach whenever possible.

(viii) *Critical exponents.* To conclude this introductory overview, we give Table 1.1.2 including the definitions of the most common static critical exponents, along with experimental values for a ferromagnet (Ni), a ferroelectric (TGS = triglycine sulfate), and the effective field results, which will be repeatedly obtained in subsequent sections.

It is well to recall that critical fluctuations at $|T - T_c|/T_c \leq 10^{-3}$ play a much more prominent role in an itinerant ferromagnet, such as Ni, than in a uniaxial ferroelectric, such as TGS.

References

1. H.E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, Oxford, 1971).
2. P. Pfeuty and G. Toulouse, *Introduction to the Renormalization Group and to Critical Phenomena* (Wiley, New York, 1978).
3. Shang-Ken Ma, *Modern Theory of Critical Phenomena* (W.A. Benjamin, Reading, MA, 1976).
4. C. Comb and M.S. Green (eds.), *Phase Transitions and Critical Phenomena* (Academic Press, London, 1972).
5. E.A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).
6. A.J. Dekker, *Solid State Physics* (Prentice Hall, Englewood Cliffs, NJ, 1962).
7. L. Onsager, *Phys. Rev.* **65**, 117 (1944).