

**Table 1.1.** Summary Table of Applications of Phase Transitions. The characteristics of the transitions are indicated in the rows and the sectors with potential applications are indicated in the columns. Concrete examples have been cited in some cases

	Electronics, Data processing	Energy, Electrical engineering	Agriculture, Food industry	Metallurgy, Mechanics	Chemistry, Pharmacy process, Engineering	Civil engineering
Latent heat		Thermal engine		Melting metal	Chemical reactor	
2nd-order Transitions	Josephson junctions, Memories	Current transmission			Supercritical	
Multicritical transitions					Oil deposits	
Metastable phases		Superheating of a liquid		Quenching of metals		Earthquakes, Thixotropy glasses
Conformation of molecules			Gels		Proteins	Clays, Cements
Nucleation, Surface properties		Evaporation of a liquid	Emulsions	Microstructures	Catalysts	Cements

## 1.7 Historical Aspect: from the Ceramics of Antiquity to Nanotechnologies

The history of the physics of phase transitions is blended with the history of materials technology and more recently with the history of thermodynamics and the physics of condensed matter.

As soon as Man mastered fire, ceramicists and metallurgists were the first to make solid materials from the phase transitions which are the basis of fabrication of ceramics and metals. Ceramics have been known in the Near East since Mesolithic times (eighth millennium before Christ), and they were first produced by baking clay-based paste in an oven. As for bronze and iron, they appeared later, in the second millennium before Christ, probably among the Hittites, as metallurgical operations require mastery of high temperatures (of the order of approximately 2000°C).

The properties of some magnetic materials were also known in antiquity. Thales of Miletus knew more than 2500 years ago that magnetite, or lodestone, attracted iron. The Chinese were undoubtedly the first to study magnetism and the long-distance action of magnets. In Europe, Peregrinus of Maricourt (1269) and W. Gilbert (1600) treated the applications of magnets and developed the first theories of magnetism.

A scientific approach to materials and phase transition problems was only possible when there was a clear concept of the notion of temperature, in fact, only since the 17th century. This notion obviously owes much to the invention

of the thermometer, with which Galileo is credited as he invented the air thermometer in 1592. The grand duke of Tuscany Ferdinand II probably made the first operating thermometer, the alcohol thermometer, in 1647; Fahrenheit developed the mercury thermometer between 1708 and 1724. Scientists such as Bacon, Descartes, Galileo, and Boyle believed that heat and its peculiar motions originated in a change of state like melting.

In the 18th century as thermal machine technology emerged with the first steam machines, meteorological phenomena began to be investigated (melting of snow, cooling of hot air by pressure reduction including condensation of water vapor, for example). With the Scottish physicist J. Black, scientists then introduced the important notions of specific heat and latent heat. Thermodynamics gradually established the body of its tenets following the work of Sadi Carnot, then J. R. Mayer, J. Joule, Lord Kelvin, and R. Clausius.

The notions of thermodynamic functions, or state function such as internal energy  $U$  and entropy  $S$  were formalized and tools were available for systematically studying phase transition phenomena at the end of the 19th century.

The systematic study of phase diagrams, particularly in metallurgy, became possible based on the knowledge of thermodynamic potentials acquired in the work of J. W. Gibbs and P. Duhem.

Moreover, the thermodynamic treatment of surface and interfacial phenomena by J. W. Gibbs opened the way to investigation of the nucleation phenomena which play a large role in phase transitions.

The existence of second-order phase transition phenomena was established for the first time in carbon dioxide,  $\text{CO}_2$ , by T. Andrews in 1869. He discovered the liquid-gas critical point in a light-scattering experiment, the phenomenon of critical opalescence. Three years later, van der Waals provided the first theoretical framework for explaining these results by proposing a state equation for real gases.

Studies of magnetism then followed the research on fluids. Pierre Curie systematically investigated high-temperature ferromagnetic properties after J. Hopkinson demonstrated the disappearance of magnetization of iron at a high temperature in 1890. Pierre Curie discovered the law bearing his name that gives the susceptibility as a function of the temperature. Pierre and Jacques Curie had previously established the foundations of a phase transition approach with symmetry principles, thus paving the way to understanding phenomena such as ferroelectricity and piezoelectricity, discovered in 1880.

Pursuing the path opened by P. Curie for studying ferromagnetism, P. Weiss advanced the hypothesis in 1907 that ferromagnetic solids could be characterized by the existence of an internal magnetic field which could account for most of the experimental results of the time: this is the molecular field approach. Paul Langevin arrived at a similar concept and results.

The progress in low-temperature physics at the end of the 19th century permitted liquefying all gases. Liquefaction of helium by Kamerlingh Onnes in 1908 opened the way to the discovery of superconductivity by the same physicist, demonstrated for the first time in mercury in 1911.

At the beginning of the 20th century, physicists had obtained a powerful investigative tool in X-rays, which allowed determining structures and their evolution. The studies of metal alloys also made an important contribution to the physics of phase transitions. G. Tammann was the first to hypothesize the existence of an ordered phase in alloys at low temperature in 1919: this was demonstrated in 1929 by C. H. Johanssen and J. O. Linde in a X-ray diffraction experiment. In 1926, Tammann and O. Heusler observed a specific heat anomaly in a bronze alloy: this was the demonstration of the critical point of the order-disorder transition. Finally, in 1934, L. Bragg and J. Williams introduced the concept of long-range order and with it paved the way to the notion of order parameter .

The analogy between the van der Waals state equation and the equation for ferromagnetics was very quickly perceived: they anticipated the analogous equations for the line of coexistence near the critical point and similar behaviors for quantities such as magnetic susceptibility and compressibility. Nevertheless, the idea of a unified approach to all of these phenomena only arose at the end of the thirties with the work of P. Ehrenfest and L. Landau, who introduced the concept of order parameter. Important theoretical advances were made in the 1920s–1930s utilizing a microscopic approach which quantum physics and quantum statistics made possible. Ising’s model (1925), first conceived for treating the case of magnetism and improved by W. Heisenberg, stimulated a very large number of studies generalizing the molecular field approach . It is necessary to note that L. Onsager was able to solve the two-dimensional Ising model for zero-field magnetism without approximation only in 1944.

Experimental methods for investigation of phase transition phenomena were again enriched beginning in 1950: precision thermometry became possible due to the progress in electronics, light scattering, and then later neutron scattering, and nuclear magnetic resonance (NMR) allowed systematically studying all phase transition phenomena in all solid and liquid materials.

The more accurate measurements of the critical points thus allowed showing that behaviors of the type predicted by the molecular field (or “van der Waals”) models poorly accounted for the experimental reality.

At the end of the 1960s, stimulated by experimental research, the approach to second-order phase transition phenomena was totally renewed. The studies by L. P. Kadanoff , C. Domb, and M. E. Fisher led to the notions of **scaling** and **universality laws** . Borrowing mathematical methods from field theory, K. G. Wilson proposed the **renormalization group** theory that allowed a unified approach to second-order phase transitions, in a certain way generalizing van der Waals’ ideas.

The technical progress made in heat treatments (utilizing lasers, for example) parallelly permitted obtaining the first metallic glasses and ceramics with increasingly small microstructures. Since the 1960s, the use of new materials (polymers, new alloys, amorphous metallic alloys, semiconductors, ceramics) in many industrial sectors (electronics, aerospace industry, automobile industry, for example) has stimulated research on phase changes in materials. We have progressively passed from microstructures whose size is of the order of the micron to structures on the nanometer scale (one-thousandth of a micron) and since the end of the 1990s, applications of nanotechnologies are feasible, for example, in electronic devices.

## Problems

### 1.1. Fluctuations

The energy of a system with fixed  $T$  and  $V$  is designated by  $E$  and its equilibrium value, which is a statistical mean, is designated by  $\langle E \rangle$ . Fluctuations in the energy are characterized by  $\langle \delta E^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle$ . Show that  $\langle \delta E^2 \rangle = C_v/k\beta^2$  with  $\beta = 1/kT$  and  $C_v$  the specific heat.

### 1.2. Fluctuations and Compressibility

Consider fluctuations in the number of particles  $N$  in a fluid of volume  $V$  around its equilibrium value  $\langle N \rangle$  and defined by  $\langle \Delta N^2 \rangle = \langle (N - \langle N \rangle)^2 \rangle$ . Using a grand-canonical distribution and the relations between  $p, \mu$  and the grand-canonical partition function, set up the relation  $\langle \Delta N^2 \rangle = \langle N \rangle \kappa_T / \kappa_T^0$ ;  $\kappa_T$  is the compressibility of the fluid and  $\kappa_T^0$  is the compressibility of an ideal gas.

### 1.3. Free Enthalpy of a Binary Mixture

The free enthalpy of a binary mixture is defined by (1.15) which is represented by a  $G(x)$  diagram, where  $x$  is the concentration of one of the constituents. If  $G_A$  and  $G_B$  designate the molar free enthalpies of the constituents in the mixture, show that the slope of the tangent at any point in the diagram is given by  $G_B - G_A$ .

### 1.4. Fluctuations and Scattering of Light

Light scattering is a very widely used technique for studying phase transitions in transparent fluids and solids (Fig. 1.15). The total scattering intensity at time  $t$  corresponding to vector  $\mathbf{k}$  is:

$$I(\mathbf{k}, t) = \langle |E(\mathbf{k}, t)|^2 \rangle$$

where  $E(\mathbf{k}, t)$  is the electric field of the scattered wave, which is associated with fluctuation of the dielectric constant  $\epsilon$  of the hypothetically isotropic medium:

$$E(\mathbf{k}, t) \propto E_0 e^{-i\omega_0 t} \delta\epsilon(\mathbf{k}, t)$$