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DEPARTMENT OF PHYSICS

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Dr. Tracey Hall
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Brigham Young University
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Dear Dr. Hall:

Thank you very much for the reference on synthesis of diamond which you recently gave me over the phone. I am enclosing a copy of the article in which I mention the subject.

Sincerely,

Melville S. Green,
Professor of Physics

MSG:let

Enc.

ARTICLE ON PHASE TRANSITIONS
FOR
ENCYCLOPEDIA OF PHYSICS

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Perhaps the most far reaching principles of physics are its conservation laws which tell us that the sum total of certain quantities, mass, energy, momentum, numbers of atoms of various species, remains constant in the transformations and vicissitudes of matter. Within the limitations imposed by the conservation laws, however, matter may undergo profound changes. Among the most striking of these changes are those called phase transitions. We need not go far from ordinary experience to encounter phase transitions. The precipitation of the water vapor of the atmosphere as rain and the subsequent evaporation of the precipitated water are both examples of phase transitions. The characteristic feature is the existence of a substance in two very different forms - in this instance a palpable liquid form and an impalpable vapor form - and the transformation of one into the other under suitable circumstances. Continuing with meteorological examples, the precipitation of water vapor in cold weather, as snow, and its subsequent evaporation or sublimation, is an example of a solid to vapor transformation, while the freezing and melting of natural bodies of water is an example of liquid to solid phase transition. Taking an example from mineralogy, carbon may exist in the familiar black amorphous form or in the beautiful crystalline form of diamond. From our human point of view these are materials of very different economic and esthetic value but from the dispassionate point of view of physics, amorphous carbon and diamond are forms of the same substance. The transformation of amorphous carbon into diamond occurs at temperatures and pressures which until recently could only be produced by geological forces, but the necessary conditions are now produced in the laboratory and in industrial processes.

In all of the examples which we have just given the transformation takes place portion by portion. The water vapor in a cloud condenses to raindrops which fall to the ground and coalesce into lakes and rivers. Diamonds are found in a matrix of amorphous carbon, suggesting that only a portion of the carbon was transformed. Such phase transitions are described as first order. In another type of phase transition the two phases are only infinitesimally different at the transition and the transformation takes place all at once. The magnetization of a permanent magnet will diminish as the temperature increases and become zero at a definite temperature, the Curie temperature. Above the Curie temperature the magnetization stays exactly zero. A more striking example is superfluid helium. Above a well-defined temperature, the lambda temperature, the flow properties of liquid helium are qualitatively no different from those of any other liquid. Immediately below the lambda temperature liquid helium acquires frictionless superflow properties while remaining only infinitesimally different from normal helium. Such phase transitions have been called, for erroneous reasons, second order phase transitions, but are more properly called continuous phase transitions. Although these two types of phase transitions are seemingly very different they are in fact aspects of the same phenomenon.

Thermodynamics

The thermodynamics of phase equilibria in which one or more phases coexist in an equilibrium system forms a very useful theoretical framework for phase transitions which helps to understand even nonequilibrium phase transition phenomena. We will confine ourselves almost exclusively to this theoretical framework in this article.

Two phases in equilibrium, denoted by I and II, may freely exchange the quantities energy, volume, and molecules of each species subject only to conservation

of the sum total of each quantity. The thermodynamic forces corresponding to each extensive or conserved quantity must be balanced. For the exchange of energy and volume this gives the condition that the temperature and pressure of each phase must be the same.

$$1) \quad T_I = T_{II},$$
$$P_I = P_{II}.$$

Moreover, corresponding to the exchange of each species i we have the condition that the corresponding chemical potential must be the same in both phases.

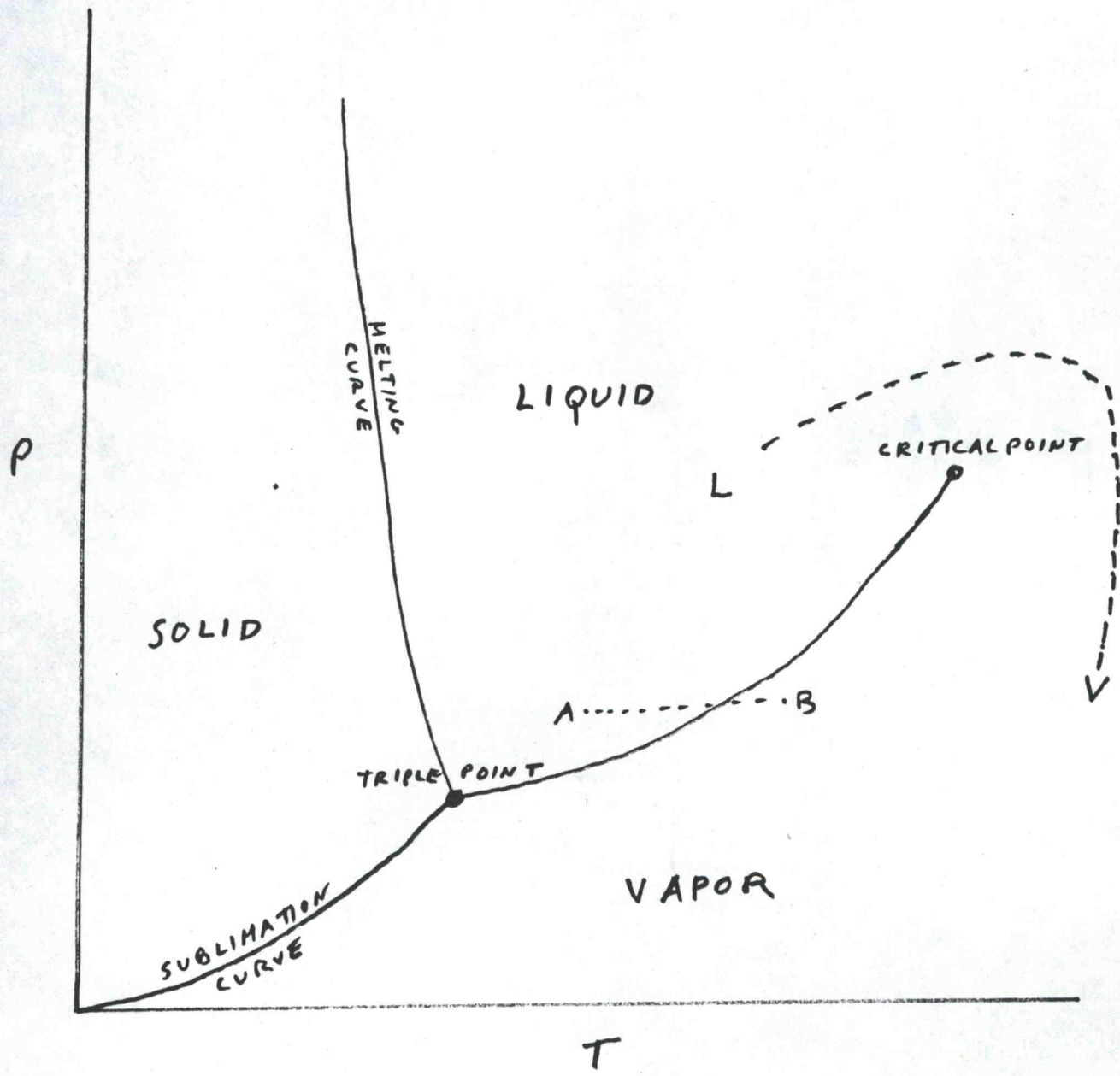
$$2) \quad \mu_I^i = \mu_{II}^i.$$

If there are more than two phases, conditions eqs.1) and 2) apply to each pair of phases. Each of the quantities μ^i in each phase may be considered to be a function of the common temperature and pressure and $r-1$ independent variables X_1, \dots, X_{r-1} , expressing composition. By a simple counting of variables and equations J. W. Gibbs arrived at his famous phase rule which determines the maximum number of phases which may coexist in equilibrium and the dimension of the manifold of coexisting states. Gibb's phase rule states

$$3) \quad r + 2 - p = c \geq 0$$

where p is the number of coexisting phases. C is the dimension of the manifold of coexisting phases. Since C may not be negative, p may not be greater than $r + 2$.

FIG. 1.



The case of a single component

The most familiar application of the phase rule is to the case of a single component. In this case the maximum number of coexisting phases is three. This occurs on a manifold of dimension zero, the triple point. Two-phase coexistence occurs along a line. In the most common case with one solid, one liquid, one vapor phase, the manifolds of coexistence in the T. P. plane are sketched in figure 1.

Caption figure 1. Manifolds of coexistence for a single component system with one liquid one vapor one solid phase. The lines of two phase coexistence are labeled with their conventional names. At a point of coexistence of two phases any quantity of one phase may be in equilibrium with any quantity of the other.

At a triple point any quantity of the three phases may coexist in equilibrium. The triple point of water may be realized in a cell in which water vapor, liquid water and ice are present in equilibrium at the same time. Such a triple point cell realizes unique temperature and pressure which is the fundamental fixed point for both the International Absolute and International Practical Scale of Temperature.

Volume change and latent heat

Figure 1 may be considered to be the projection on the T. P. plane of the surface $\mu(T,P)$ where μ is the chemical potential of the single species. To each temperature and pressure not on a manifold of coexistence corresponds a unique phase as indicated in figure 1. $\mu(T,P)$ must be continuous according to the conditions of equilibrium (eqs. 1 and 2) but its first derivatives need not be. The differential of $\mu(T,P)$ is

$$d\mu = -s dT + \nu dP \quad \text{or,}$$

4)

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -s, \quad \left(\frac{\partial \mu}{\partial P}\right)_T = \nu.$$

where s and ν are the entropy and volume per mole respectively. Thus the discontinuity of the first partial derivatives of μ which is the origin of the adjective, first order, is an expression of the fact that the density and other properties of two coexisting phases are different. The change of entropy in a phase change has a simple calorimetric meaning. Since a reversible phase transformation occurs at a constant temperature the change in entropy per mole is simply the heat absorbed in the process divided by the temperature.

$$5) \quad \Delta S = S_{II} - S_I = \frac{L}{T}.$$

where S_I , S_{II} are the molar entropies of phases I and II and L is the heat absorbed at constant temperature or latent heat of the process. (Latent because not concomitant with a change in temperature).

Clapeyron-Clausius equation

The slope of a coexistence line is related to the entropy change and volume change by an equation which may be derived by differentiating the equilibrium condition eq. 2.

$$6) \quad \frac{dP}{dT} = \frac{S_{II} - S_I}{V_{II} - V_I} = \frac{L}{T \Delta V}$$

where $\frac{dP}{dT}$ is the slope of the coexistence curve. Since sublimation, vaporization and melting all represent transitions from a less to a more disordered state the statistical mechanical relation - entropy is equivalent to disorder - explains the fact that the latent heats of these phase changes are positive. Sublimation and vaporization both involve positive volume changes so the corresponding coexistence curves have positive slopes. The molar volume of a liquid and its corresponding solid however are very nearly the same and the volume change may be slightly positive or slightly negative. Water is one of the relatively few cases where the liquid is denser than the solid. This circumstance explains the natural phenomenon that ice forms on the surface of a lake as well as the fact that water melts under pressure.

Continuity of state and the critical point

As indicated in figure 1 the vapor pressure curve has a definite end point, the critical point. Thus even though the liquid and vapor phases are physically

quite distinct the corresponding domains in fig. 1 are connected. The solid region on the other hand seems to be completely disjoint from the fluid region. It is thus physically possible to transform a liquid into a vapor without a phase change by following a reversible process. (The line L V in fig. 1). This is the continuity of the liquid and vapor states.

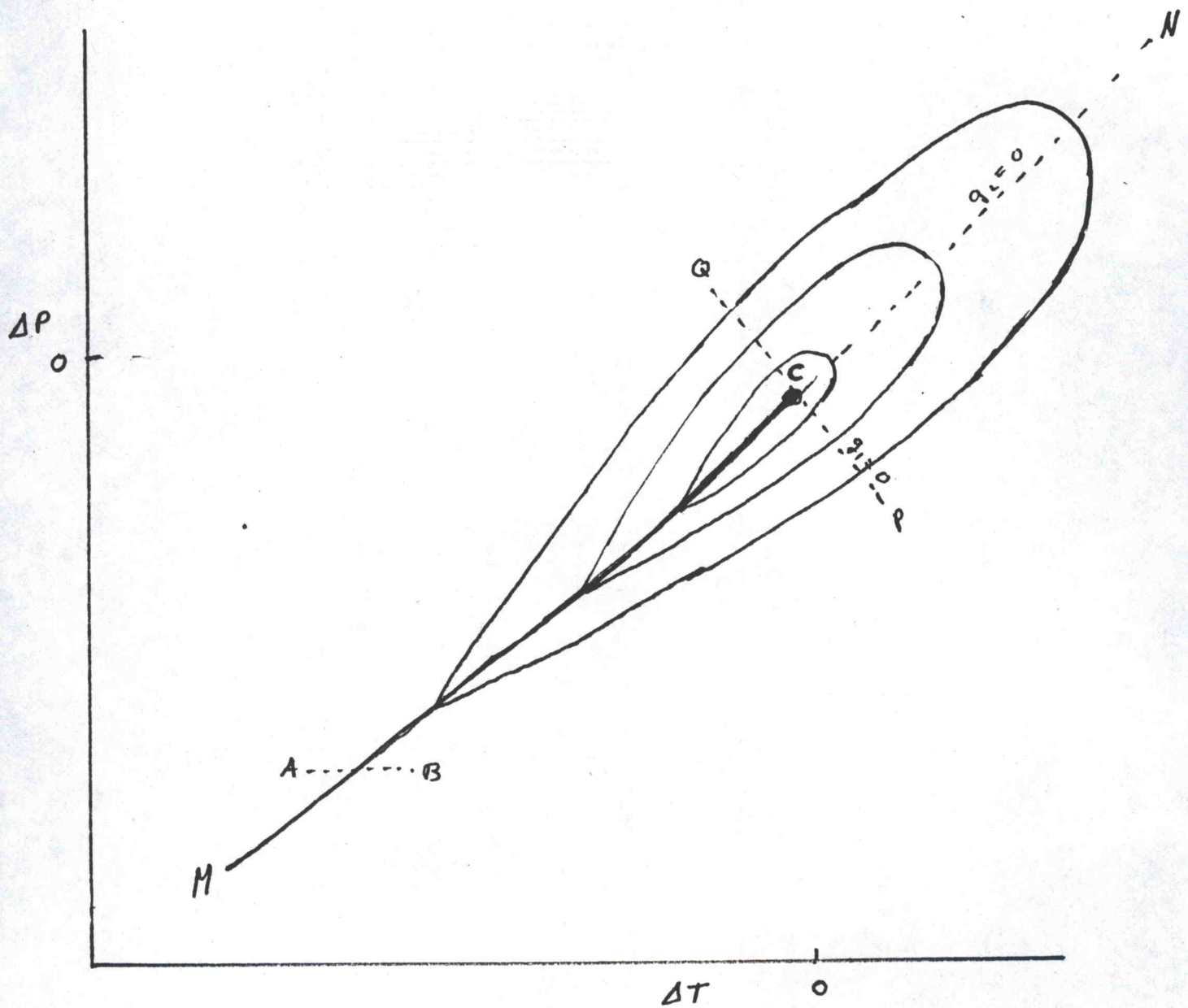
Along the coexistence curve the difference in density, entropy density and other properties between the liquid and vapor phases diminishes and disappears entirely at the critical point. An important practical meaning of the critical point may be seen from fig. 1. For temperatures below the temperature of the critical point (critical temperature) a vapor may be liquified by compressing without cooling; above the critical temperature this is not possible. Thus fluids with low critical temperatures are difficult to liquify. Helium, with a critical temperature of 5.1°K was liquified by Kamerlingh-Onnes only in 1908. The evanescence of the distinction between liquid-vapor in the neighborhood of the critical point is the cause of the very striking phenomena of critical opalescence. The natural thermal fluctuations produce temporary liquid-like or vapor-like regions throughout the fluid which are large enough to scatter light and cause the otherwise medium substance to become cloudy or opalescent.

Critical Singularities

The surface $\mu(T,P)$ becomes singular in the mathematical sense at the critical point. In fig. 2 are sketched a sequence of curves representing the intersection of this surface with a series of planes parallel to its tangent plane at the critical point. The surface is concave downward.

Fig. 2

FIG 2



Caption figure 2. Critical singularity of the surface $\mu(T, P)$. The closed curves represent the intersection of this surface with a sequence of planes parallel to the tangent plane at the critical point. $M C N$ is the line $g_2 = 0$, $Q C P$, $g_1 = 0$.

$\mu(T,P)$ and its first partial derivatives are continuous at the critical point but its second partial derivatives are infinite there. This means that the specific heat at constant volume, the isothermal compressibility as well as other important physical quantities become infinite at the critical point.

Near the critical point $\mu(T,P)$ may be represented in the so-called scaling form

$$7) \quad \mu(T,P) = \mu_c - s_c \Delta T + v_c \Delta P + |g_1|^{2-\alpha} F_{\pm} \left(\frac{g_2}{|g_1| \Delta} \right)$$

where s_c, v_c and μ_c are the critical entropy, volume per mole and chemical potential and g_1 and g_2 , called scaling fields, may be taken to be linear combinations of $\Delta T = T - T_c$ and $\Delta P = P - P_c$. The indices \pm refer to the cases $g_1 \geq 0, g_1 < 0$ respectively. The line $g_2 = 0$ is tangent to the vapor pressure curve and to the critical isochore (curve of constant volume equal to critical volume). $2-\alpha \approx 1.9, \Delta \approx 1.5$. The line $g_1 = 0$ has a less obvious meaning. One of the important recently discovered features of the critical region is the principle of universality. For fluids this means that the function F_{\pm} is the same for all fluids. The only features of the singularity which changes from fluid to fluid are coefficients of ΔT and ΔP in g_1 and g_2 and the parameters of the tangent plane at the critical point, i.e., s_c, v_c, μ_c .

Continuous Phase Transitions

The transformation from one phase to another usually takes place along a path (AB in fig. 1) which crosses the coexistence curve. When the system reaches the coexistence curve along such a path, it hesitates, as it were, while small

portions of the system are transformed successively from one phase to the other. Since the singularity in the coexistence curve is experimentally a simple jump singularly in the derivatives of $\mu(T,P)$ there is no observable precursor or after-effect of the transition. Along the curve $g_2 = 0$ (MCN in fig. 2), the phenomenon looks very different. For a fluid this path may be easily achieved by confining the system to vessel of fixed volume. As g_1 is diminished through positive values to zero the system consists of one fluid phase. At the critical point and below $g_1 \leq 0$ the system divides up without any hesitation into equal amounts of liquid phase and vapor phase which in this region are only slightly different from each other. Since the path $g_2 = 0$ passes right through the singularity, the specific heat and compressibility tend to infinity both above and below the transition.

For a fluid the path $g_2 = 0$ is only one among many achievable paths and the system clearly consists of two phases separated by gravity, for $g_1 < 0$. For certain systems the most natural path or even the only physically possible path is along $g_2 = 0$. This may come about for reasons of symmetry or other reasons. Moreover for the same reasons the state of the system for $g_1 < 0$ may not be easily identifiable as a mixture of two phases but appears to be a single albeit somewhat anomalous phase. The properties of this anomalous mixed phase for $g_1 < 0$ approach those of the single phase, $g_1 > 0$, continuously. For this reason such transitions are called continuous phase transitions. An example is the case of an anti-ferromagnet such as rubidium manganese fluoride $RbMnF_3$ where above temperature of $83.02^\circ K$, called the Néel temperature the magnetic moments of the manganese ions are oriented randomly but below the Néel temperature the

moments are oriented alternately parallel or anti-parallel to some fixed direction

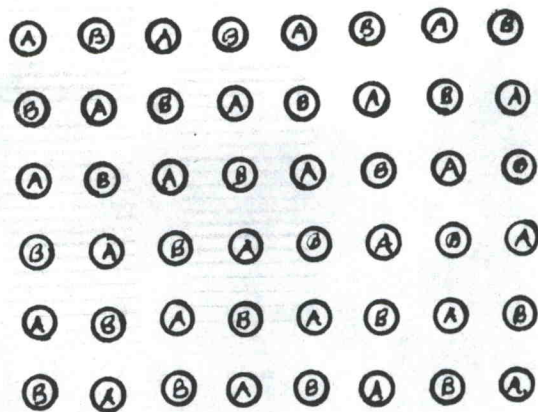


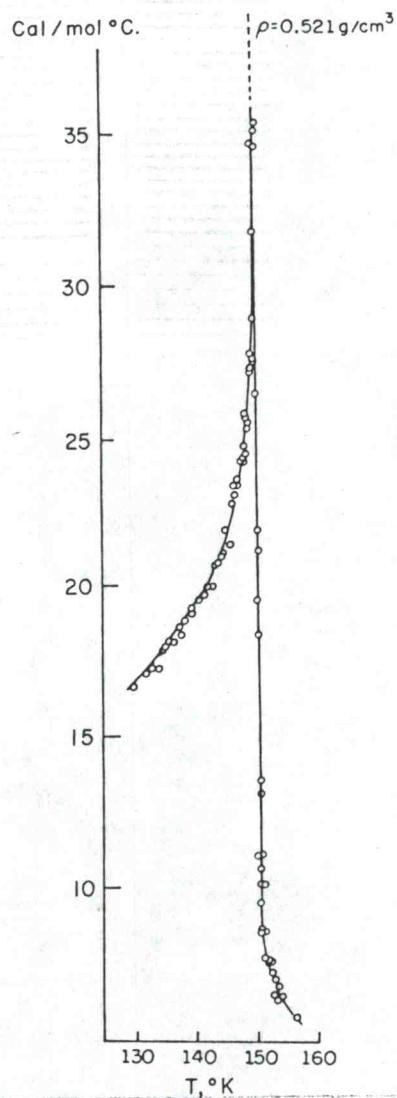
Fig. 3

The situation is illustrated in fig. 3 which represents the lattice of manganese ions in say the 001 plane. This lattice may be divided into two interpenetrating cubic lattices of A sites and B sites. The exchange interaction between manganese ions favors nearest neighbors whose magnetic moments are oppositely oriented. Above the Néel temperature this bias of the interaction is manifested only locally so that the nearer neighbors of any manganese ion are likely to have oppositely oriented moments but the further neighbors are random. This is called local order. Below the Néel temperature the effect of this bias extends cooperatively throughout the crystal and the moments on the whole A and on the whole B lattice are each oriented in the same way but opposite to each other. This situation may be realized in two distinct but equivalent ways, A up, B down and B, up, A down. These two realizations may be taken to be two phases in equilibrium. Since these two phases differ physically only by a translation of the lattice by one primitive lattice vector, there is no macroscopic agency or field which favors one over the other. Thus the system is restricted to a completely symmetric state which above the Néel temperature is the state of zero average moment on each site but below the Neel temperature is

an equal mixture of both phases. We are confined to the line $g_2 = 0$. Because this line passes through the Neel point (critical point) the specific heat becomes infinite giving rise to the characteristic signature of a continuous phase transition, specific heat curve which is reminiscent of the Greek letter λ (fig. 4). On the other hand properties which depend only on the first derivatives of the thermodynamic potential such as the magnetization M_s , of either one of the sublattices are continuous.

Fig. 4

Other physical systems exhibiting continuous phase transitions are ferromagnets and superfluid helium. In the former the phenomena are somewhat complicated by the effect of magnetic dipole forces which make the phenomena somewhat dependent of the shape of the sample, but these may be minimized in appropriately shaped samples. In the case of the normal to superfluid transition in liquid helium, the external field which would take us off the line $g_2 = 0$ is zero as a consequence of a very fundamental symmetry principle, gauge symmetry, whose breaking would involve the creation or destruction of helium atoms. Although the examples of continuous phase transitions discussed above have the same basic thermodynamic description they are physically very different phenomena.



Caption figure 4 Variation of C_v of argon with T along critical isochore.

Source: Reference 7 Vol. 5B after Bagatskii, M., Voronel, A., Gusak, V., Sov. Phys. JETP 25 72 (1963).

Order Parameter

Associated with a continuous phase transition is a scalar or vector parameter which determines the physical nature of the transition. It has the value zero in the random state (usually above the transition temperature) and acquires non-zero values in the ordered state (usually below the transition). In the case of a fluid the order parameter is a scalar, the difference in density between the liquid and vapor phase. In the case of an isotropic ferromagnet or antiferromagnet, the order parameter is a three dimensional vector quantity, the magnetization or the sublattice magnetization. In the case of superfluidity (also superconductivity) the order parameter is a complex quantity with a magnitude and phase angle which may be interpreted as the wave function of the finite fraction of the particles which have zero momentum. The superflow properties may be considered to be a manifestation of the fact that a wave function with zero momentum cannot be localized. The order parameter also determines the universality class of the transition. Continuous phase transitions which have order parameters with the same tensorial character and the same space dimension belong to the same universality class, i.e., have the same singularity in the thermodynamic potential. When the order parameter is multi-dimensional we note that the ordered state must be considered to consist of a mixture of not merely two but of a continuous infinity of phases in equilibrium.

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