

Thus, we can define a *spin* (or Ising) *pressure* by $p_I = -(\partial A_I / \partial V)_T$; this contribution to the total pressure is directly related to the Ising energy U_I by

$$p_I = kT \left(\frac{\partial \ln Q_I}{\partial J} \right)_T \frac{dJ}{dV} = \left(\frac{d \ln Q_I}{dH} \right) \frac{dJ}{dV} = -\frac{U_I}{NJ} \frac{dJ}{dv}, \quad (6)$$

where $v = V/N$ is the volume per lattice site. Note that U_I has a negative value in the ordered phase and goes to zero as the spins disorder.

INSTABILITY AND HYSTERESIS

At a given temperature T a system is stable, at least locally, if the Helmholtz free energy satisfies the condition $(\partial^2 A / \partial V^2)_T \geq 0$. For the model considered above, this stability condition requires that

$$-(\partial p_{al} / \partial v)_T - (\partial p_I / \partial v)_T \geq 0, \quad (7)$$

where $(\partial p_I / \partial v)_T$ is found from Eq. (6) to be

$$(\partial p_I / \partial v)_T = (T/NJ^2) C_I (dJ/dv)^2 - (U_I/NJ) (d^2 J / dv^2). \quad (8)$$

Since $(\partial p_{al} / \partial v)_T$ is related to $\beta_{al} T$, the isothermal compressibility of the disordered lattice, by

$$1/\beta_{al} T = -v (\partial p_{al} / \partial v)_T \quad (9)$$

one can write the stability condition as

$$\frac{1}{\beta_{al} T} - \frac{vT}{NJ^2} C_I \left(\frac{dJ}{dv} \right)^2 - \frac{vU_I}{NJ} \left(\frac{d^2 J}{dv^2} \right) \geq 0. \quad (10)$$

Now $1/\beta_{al} T$ will in general have a finite positive value which is a slowly varying function of temperature, while J and its derivatives with respect to v will be finite non-zero quantities which are independent of temperature. The Ising internal energy will also be finite at all temperatures; but the configurational heat capacity at constant volume, C_I , is known to approach very large values in the vicinity of the critical point. The behavior of C_I is the crucial factor. If C_I approaches $+\infty$ at the critical temperature, there must be an instability near that point unless the particle lattice is completely incompressible (in which case, $1/\beta_{al} T = +\infty$). This result depends only on our assumption of weak coupling in the model.

For the two-dimensional Ising model an exact analytical expression for Q_I (and thus C_I) is available,¹ and C_I is known to have a logarithmic singularity at T_c . Equations (6)–(10) are still valid in two dimensions if v is replaced by σ , the surface area per lattice site, and p is understood to be a surface pressure defined by $-\partial A / \partial (N\sigma)$. In this case, the instability of a compressible lattice in the immediate vicinity of its critical point follows directly from Eq. (10). This instability will cause the system to undergo a spontaneous first-order phase transition across the unstable region. Associated with this first-order transition is the possibility of hysteresis. To illustrate these conclu-

sions we discuss below several different aspects of the behavior of a two-dimensional model. In this case, Eq. (6) allows us to easily calculate the Ising pressure p_I from the known expression¹ for U_I if J and $dJ/d\sigma$ are specified. For a ferromagnet, J is simply related to the critical temperature ($J = 0.44069 kT_c$) and it is physically reasonable to expect that $dJ/d\sigma < 0$. Let us represent J by the form α/σ^n , (where n is a small integer) as an illustrative example. A typical disordered-lattice pressure will be represented over a small range of σ by

$$p_{al} = a_0 + a_1 T - b\sigma, \quad (11)$$

where a_0 , a_1 , and b are positive constants.

Constant External Pressure

For a system at equilibrium under an external applied pressure, it is necessary that $p_{ext} = p_{al} + p_I$. We treat the simplest case of zero external pressure, for which $p_I = -p_{al}$. Figure 1 shows a plot of p_I and $-p_{al}$ against σ at several temperatures $T_1 < T_2 < \dots < T_6 < T_7$. An intersection of the two appropriate isotherms will give the equilibrium area σ under zero external pressure if the stability condition (7) is satisfied (that is, if the slope of $-p_{al}$ is greater than that of p_I). Now consider the change in σ with T for $p_{ext} = 0$. As the temperature increases from T_1 to T_5 , σ can increase continuously from σ_1 to σ_5 (Points 1 to 5 on Fig. 1), but as $T \rightarrow T_5$ from below the system becomes unstable ($\partial^2 A / \partial \sigma^2 = 0$) at Point 5 and there must be a first-order change in area from σ_5 to σ_5' . On further heating, σ increases continuously from σ_5' to σ_7 . However, on cooling from T_7 to T_3 the area can decrease smoothly from σ_7 to σ_3' . As $T \rightarrow T_3$ from above the instability occurs at Point 3' and there is a first-order change from σ_3' to σ_3 . Below T_3 , σ decreases smoothly on cooling. Thus, there can be a hysteresis loop near the critical point with a first-order jump in σ at T_5 on heating and a first-order drop in σ at T_3 on cooling; this is shown schematically in an inset on Fig. 1. The values T_3 and T_5 determine the maximum width of this loop since the system becomes mechanically unstable at Points 5 and 3'. Actually, there is a temperature T_4 for which the free energy at Point 4 equals that at Point 4'; complete thermodynamic equilibrium would give a first-order transition at T_4 and no hysteresis. The region between 4 and 5 on heating or 4' and 3' on cooling is only metastable. It is easy to show that a Maxwell equal-area rule is valid for determining T_4 in this system.

The lower inset on Fig. 1 presents a schematic sketch of the temperature dependence of $1/\beta^T$ in the critical region. On warming, as T_5 is approached from below, $1/\beta^T$ approaches zero and then jumps to the value B after the first-order transition occurs. On cooling, as T_3 is approached from above, $1/\beta^T$ vanishes and jumps to the value A after the transition. If the system is in complete thermodynamic equilibrium, $1/\beta^T$ never van-

FIG. 1. Ising model at vanishing external pressure. The figure shows a plot of p_I and $-p_{al}$ against σ at several temperatures $T_1 < T_2 < \dots < T_6 < T_7$. The figure is drawn to show typical expansion and contraction isotherms 1 and 2, respectively, and the critical point is shown at Point 5.

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