3.E. Superconductors

In 1911, K.Onnes observed a sudden drop to zero in the electrical resistivity ρ of mercury as the temperature T fell below $4.2\,K$ [see Fig.3.11 in Reichl's text]. The phenomenon, called superconductivity, was subsequently observed in all metals as T falls below a critical temperature T_C that depends on the material.

According to the Ohm's law,

$$\boldsymbol{J} = \sigma \boldsymbol{E} = \frac{1}{\rho} \boldsymbol{E} \tag{3.50}$$

where $\boldsymbol{J}$ is the electric current density, $\boldsymbol{E}$ the electric field, and $\sigma = \rho^{-1}$ the electrical conductivity.

A conductor with $\rho = 0$ or $\sigma = \infty$ is called perfect and can sustain a finite current in the absence of an electric field. A superconductor is therefore a perfect conductor.

Consider now the Faraday's law in Gaussian units,

$$\nabla \times \boldsymbol{E} = -\frac{1}{c} \frac{\partial \boldsymbol{B}}{\partial t} \tag{3.51}$$

$$= \rho \nabla \times \boldsymbol{J} \qquad \text{[(3.50) used.]} \tag{3.51a}$$

where $\boldsymbol{B}$ is the magnetic induction.

Since superconductors are perfect conductors, (3.51a) implies

$$\frac{\partial \boldsymbol{B}}{\partial t} = 0 \qquad \rightarrow \qquad \boldsymbol{B} = \text{const} \tag{3.51b}$$

in, and during the transition to, the superconducting state.

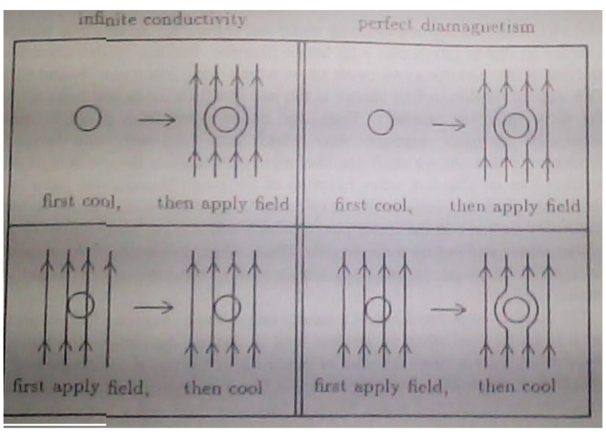

Fig.3.12.

Therefore [see Fig.3.12]

1. If a sample is first cooled below T_C in the absence of any magnetic field, then $\boldsymbol{B} = 0$ inside the sample when an external magnetic field is applied.
2. If the sample is cooled below T_C in an external magnetic field, then $\boldsymbol{B} \neq 0$ inside the sample.

Thus, the superconducting state depends on the history of the system, and hence not a thermodynamic equilibrium state.

However, measurements done on tin by Meissner & Ochsenfeld showed that $\mathbf{B} = 0$ in both cases [see Fig.3.12]. This is called the Meissner effect. Consider now the Ampere's law,

$$\nabla \times \mathbf{H} = \frac{4\pi}{c} \mathbf{J} = \frac{1}{\mu} \nabla \times \mathbf{B} \qquad [\, \mathbf{B} = \mu \mathbf{H} \text{ used.} \,] \qquad (3.51c)$$

where $\mathbf{H}$ is the magnetic field and μ is the magnetic permeability. A material is

paramagnetic	if	$\mu > 1$
diamagnetic	if	$\mu < 1$
perfectly diamagnetic	if	$\mu = 0$

From (3.51c), we have

$$\mathbf{J} \neq 0 \quad \& \quad \mathbf{B} = 0 \quad \rightarrow \quad \mu = 0$$

so that the superconductor is also a perfect diamagnet. In other words, the constant in (3.51b) is exactly zero. With this additional requirement, the superconducting state becomes independent of the history of the system, and is hence a thermodynamic equilibrium state.

In the Bardeen-Cooper-Schrieffer (BCS) theory, the superconducting state is a coexisting mixture of normal electrons and a Bose condensation, in the momentum space, of the Cooper pairs [a Cooper pair is a bosonic bound state of two electrons with opposite spins and momenta]. Since the electrons in the condensate are now in a single macroscopic quantum state, their movement is no longer impeded by the scattering with impurities or phonons. Hence, $\rho_s = 0$ for the condensate. Let ρ_n be the resistivity for the normal electrons. Since both kinds of electrons exist in the same real space that is the conductor, the total resistivity ρ is given by the parallel connection rule as

$$\frac{1}{\rho} = \frac{1}{\rho_n} + \frac{1}{\rho_s} \qquad \rightarrow \qquad \rho = 0$$

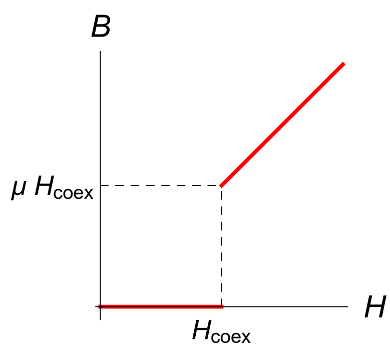

Fig.3.13.

Superconductivity can be destroyed by a sufficiently large magnetic field $\mathbf{H}$. As can be seen in Fig.3.13.,

$$B = \begin{cases} 0 & \text{if } H < H_{\text{coex}}(T) \qquad \text{superconducting state} \\ \mu H & \text{if } H > H_{\text{coex}}(T) \qquad \text{normal state} \end{cases} \qquad (3.52)$$

where H_{coex} is the temperature dependent critical field strength that marks the transition between the superconducting and normal phases. Thus, $H_{\text{coex}}(T)$ is the coexistence curve in the T-H plane. Experiments found that for Type-I superconductors, which includes all pure metals,

$$H_{\text{coex}}(T) = H_0 \left(1 - \frac{T^2}{T_C^2}\right) \qquad \text{for } T \leq T_C \qquad (3.53)$$

where T_C is the critical temperature at $H = 0$ and $H_0 = H_{\text{coex}}(0)$ [see Fig.3.14].

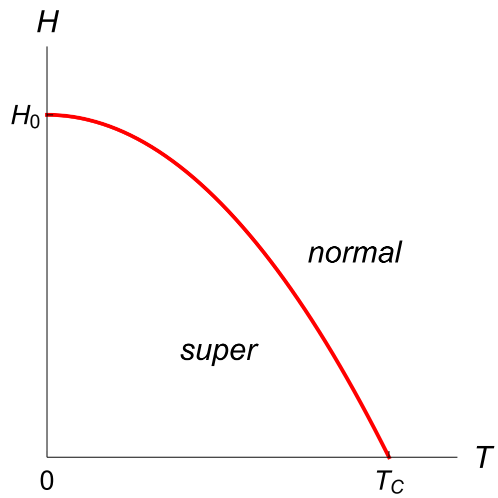

Fig.3.14. Coexistence curve.

Behavior of the system in the coexistence region is similar to that of a PVT system, with

$H \leftrightarrow P$ and $B \leftrightarrow V$

The magnetic energy density is given by

$$d\,u_M = \frac{1}{4\pi} \boldsymbol{H} \cdot d\boldsymbol{B}$$

Thus, for $\boldsymbol{H} \,//\, \boldsymbol{B}$, the Gibbs energy density, which is proportional to the chemical potential, becomes

$$d\,g = -s\,d\,T - \frac{1}{4\pi} B\,d\,H \qquad (3.57)$$

Since the chemical potentials of the two phases must be equal in the coexistence region,

$$-s_n\,d\,T - \frac{1}{4\pi} B_n\,d\,H_{\text{coex}} = -s_s\,d\,T - \frac{1}{4\pi} B_s\,d\,H_{\text{coex}} \qquad (3.45)$$

$$= -s_s\,d\,T \qquad [\, B_s \equiv 0 \,]$$

where $s = \frac{S}{V}$ is the entropy density, and the subscripts n & s indicate the normal & superconducting phases, respectively. Hence, the Clausius-Clapeyron equation is [c.f. (3.14) in §3.D.2]

$$\frac{d\,H_{\text{coex}}}{d\,T} = -4\pi \frac{s_n - s_s}{B_n}$$

$$= -4\pi \frac{\Delta h_{s\,n}}{T\,B_n} = -\frac{4\pi\,\Delta h_{s\,n}}{T\,\mu\,H_{\text{coex}}} \qquad (3.55)$$

where $\Delta h_{s\,n}$ is the enthalpy (or latent heat absorbed) of the (1st order) transition from super to normal state, and $\mu \approx 1$ is the permeability of the normal metal.

Using (3.53), we have

$$\frac{d\,H_{\text{coex}}}{d\,T} = -2\,H_0 \frac{T}{T_C^2} \qquad (3.55a)$$

and (3.55) gives

$$\Delta h_{s\,n}(T) = -\frac{\mu\,H_{\text{coex}}(T)}{4\pi} T \frac{d\,H_{\text{coex}}}{d\,T}$$

$$= \frac{\mu\,H_{\text{coex}}(T)}{2\pi} H_0 \frac{T^2}{T_C^2} \qquad (3.55b)$$

Since [see (3.53)]

$$H_{coex}(T_C) = 0 \qquad (3.55c)$$

(3.55b) gives

$$\Delta h_{sn}(T_C) = 0$$

so that the transition at $T = T_C$ is continuous.

The change in heat capacity per unit volume is

$$(c_n - c_s)_{coex} = T \left.\frac{\partial (s_n - s_s)}{\partial T}\right|_{coex}$$

$$= \frac{d \Delta h_{sn}}{d T}$$

$$= \frac{\mu H_0}{2\pi}\left(\frac{d H_{coex}}{d T}\frac{T^2}{T_C^2} + H_{coex}\frac{2T}{T_C^2}\right) \qquad \text{[(3.55b) used.]}$$

$$= \frac{\mu H_0}{2\pi}\left[-2 H_0 \frac{T}{T_C^2}\frac{T^2}{T_C^2} + H_0\left(1 - \frac{T^2}{T_C^2}\right)\frac{2T}{T_C^2}\right] \qquad \text{[(3.53) \& (3.55a) used.]}$$

$$= \frac{\mu H_0^2}{\pi T_C}\left(\frac{T}{T_C} - 2\frac{T^3}{T_C^3}\right) \qquad \text{for } T \le T_C \qquad (3.56)$$

For $\frac{T}{T_C} << 1$, we have $(c_n - c_s)_{coex} > 0$. However, this difference diminishes as T rises until

$$(c_n - c_s)_{coex} = 0 \qquad \text{at } T = \frac{1}{\sqrt{2}} T_C$$

For still higher T, $(c_n - c_s)_{coex} < 0$ with

$$(c_n - c_s)_{coex} = -\frac{\mu H_0^2}{\pi T_C} \qquad \text{at } T = T_C \qquad (3.56a)$$

Now, since the coexistence region shrinks to a single point at $T = T_C$, the conductor is completely normal (superconducting) for T slightly larger (smaller) than T_C. Hence, the heat capacity of the conductor has a finite discontinuity across $T = T_C$ as given by (3.56a).

Integrating (3.57) at a fixed T gives

$$g(T, H) - g(T, 0) = -\frac{1}{4\pi}\int_0^H B\, dH \qquad (3.58)$$

For the normal state (or phase), (3.58) gives

$$g_n(T, H) - g_n(T, 0) = -\frac{\mu}{4\pi}\int_0^H H\, dH = -\frac{1}{8\pi}\mu H^2 \approx -\frac{1}{8\pi}H^2 \qquad (3.59)$$

In particular,

$$g_n(T, H_{coex}) - g_n(T, 0) \approx -\frac{1}{8\pi}H_{coex}^2(T) \qquad (3.59a)$$

For the superconducting state, (3.58) gives

$$g_s(T, H) - g_s(T, 0) = 0 \qquad (3.60)$$

In the coexistence region,

$$g_n(T, H_{coex}) = g_s(T, H_{coex}) \qquad (3.61)$$

so that (3.59a) gives

$$g_s\,(T, H_{\text{coex}}) - g_n(T, 0) \approx -\frac{1}{8\,\pi}\,H^2_{\text{coex}}(T)$$

which, with the help of (3.60), becomes

$$g_s(T, 0) - g_n(T, 0) \approx -\frac{1}{8\,\pi}\,H^2_{\text{coex}}(T) \qquad (3.62)$$

i.e.,

condensation energy density ≈ magnetic energy density of $H_{\text{coex}}(T)$

Note that putting (3.55c) into (3.62) gives

$$g_s(T_C, 0) = g_n(T_C, 0)$$

as expected.

Code

```
In[ ]:= BF[H_] := { 0   H < 1
                  { H   H > 1

(* Fig.3.13 *)
Plot[BF[H], {H, 0, 2},
     PlotStyle → {Thick, Red},
     AxesLabel → {"H", "B"},
     AspectRatio → Automatic,
     Ticks → {{0, {1, "Hcoex"}}, {0, {1, "μ Hcoex"} }},
     TicksStyle → Directive[14],
     Epilog → {Dashed, Line[{{0, 1}, {1, 1}}], Line[{{1, 0}, {1, 1}}]}
]

In[1]:= Hco[T_] := 1 - T^2

In[2]:= (* Fig.3.14 *)
Plot[ Hco[T], {T, 0, 1},
     PlotStyle → {Thick, Red}, PlotRange → 1.2 {{0, 1}, {0, 1}},
     AxesLabel → {"T", "H"},
     AspectRatio → Automatic,
     Ticks → {{0, {1, "TC"}}, {{1, "H0"} }},
     TicksStyle → Directive[14],
     Epilog → {Text["super", {.5, .3}], Text["normal", {.9, .6}]}
]
```