8.08 Statistical Physics II

Ferromagnetic and Superconducting Phase Transitions
(Dated: February 28, 2011)

1. Consider a type I superconducting material with a parabolic coexistence curve separating the (uniform) superconducting and normal phases. H is teh external magnetic field, and T is the temperature. Ignore the tiny magnetization of the normal phase. The critical field H_c is given by

$$H_c = H_0 + aT + bT^2$$

   (a) Why must the coefficient a be zero?

   (b) Calculate the latent heat per unit volume as a function of T along the coexistence curve in terms of H_0 and T_c.

   (c) Calculate the discontinuity in the specific heat per unit volume at constant H along the coexistence curve.

Solution

(a) When the differential of the energy is $dE = TdS - PdU$, the Clapeyron equation is

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

Similarly for $dE = TdS + HdM$ the Clapeyron equation is

$$\frac{dH}{dT} = -\frac{\Delta S}{\Delta M}$$

From the third law of Thermodynamics $S \to 0$ on both sides of the transition as $T \to 0$, $\Delta S \to 0$ as well, so

$$\frac{dH}{dT} \to 0 \ , \ T \to 0$$

which means that $a = 0$.

(b) The Clapeyron equation can be written as

$$\frac{dH}{dT} = -\frac{L}{T\Delta M}$$

, where $L = T\Delta S$ is the latent heat. Taking the derivative of the critical field with respect to temperature we get

$$L = -2bT^2\Delta M$$

At $T = T_c$,

$$H_c = H_0 + bT_c^2 \Rightarrow b = \frac{-H_0}{T_c^2}$$

Plugging this back into the expression for the latent heat gives

$$L = 2H_0\left(\frac{T}{T_c}\right)^2 \Delta M = 2H_0\left(\frac{T}{T_c}\right)^2 M_{super}$$

Now let's find M_{super}. Inside a Type I superconductor $B = H + 4\pi M = 0 \Rightarrow M_{super} = -\frac{H_c}{4\pi}$
Finally the latent heat is

$$L = -\frac{H_0^2}{2\pi}\left[\left(\frac{T}{T_c}\right)^2 - \left(\frac{T}{T_c}\right)^4\right]$$

(c)

$$\Delta C = T\left[\left(\frac{\partial S_s}{\partial T}\right)_H - \left(\frac{\partial S_n}{\partial T}\right)_H\right] = T\frac{\partial \Delta S}{\partial T}$$

Relating this to the latent heat we get

$$\Delta C = T\frac{\partial (L/T)}{\partial T}$$

Taking the derivative leads to

$$\Delta C = -\frac{H_0^2}{2\pi}\left[\frac{T}{T_c^2} - \frac{3T^3}{T_c^4}\right]$$

2. Helium atoms can be adsorbed on the surface of the metal, an amount of work Φ is being necessary to remove a helium atom from the metal surface to infinity. The helium atoms are completely free to move, without mutual interaction, on the two-dimensional metal surface. If such a metal surface is in contact with helium gas at pressure P, and the whole system is in equilibrium at temperature T, what is the mean number of atoms adsorbed per unit area of the metal surface? Express your answer in terms of quantities given in the problem, and fundamental contacts.

   Solution:

   The differential of the free energy of the system is

$$dF = dF_g + dF_s = \mu_s dN_s + \mu_g dN_g$$

   . $dN_g = -dN_s$ so $\mu_s = \mu_g$ or $\frac{\partial F}{\partial N_g} = \frac{\partial F}{\partial N_s}$

   The partition function is $Z = Z_g Z_s$ where

$$Z_g = \frac{1}{N_g!}\left[\int \frac{d^3pd^3r}{h^3} e^{-mv^2/2kT}\right]^{N_g} = \frac{[V(2\pi mkT/h^2)^{3/2}]^{N_g}}{N_g!}$$

   and

$$Z_s = \frac{1}{N_s!}\left[e^{\phi/kT}\int \frac{d^spd^sr}{h^3} e^{-mv^2/2kT}\right]^{N_s} = \frac{[e^{\phi/kT}(2\pi AmkT/h^2)]^{N_s}}{N_s!}$$

   The free energy is

$$F = -kTlnZ = -kT[N_g ln(V(2\pi mkT/h^2)^{3/2})] + N_s ln[e^{\phi/kT}(2\pi AmkT/h^2)] - ln(N_s!) - ln(N_g!)$$

   Using Stirling's approximation and setting the chemical potentials equal, we get

$$\frac{N_s}{N_g} = \frac{Ah}{V}\left(\frac{1}{2\pi mkT}\right)^{1/2} e^{\phi/kT}$$

   The number of atoms adsorbed per unit area is

$$n = \frac{hP}{kT}\left(\frac{1}{2\pi mkT}\right)^{1/2} e^{\phi/kT}$$

3. Barium titanate is an ionic crystal hat exhibits a ferroelectric transition at $T_c = 381\ K$. Above the Curie temperature, $BaTiO_3$ has cubic symmetry with a unit cell. Below T_c, $BaTiO_3$ develops a spontaneous electric polarization $\vec{P}$.

   (a) Construct the Landau free energy function for the ferroelectric transition through fourth order in the order parameter P

(b) What are the allowed directions of P, relative to the crystal axes, if the transition is second order?

(c) Sketch a plausible form for the phase diagram for $BaTiO_3$in the pressure-temperature plane based on the free energy function constructed in (a). Label the order of all transition lines.

(d) The appearance of the electric polarization P for $T < T_c$ must be accompanied by displacements of the symmetric arrangement of the ions. Thus, ferroelectricity is not simply described by a single order parameter, the free energy function must also depend upon the strain. Assuming the distorted lattice has tetragonal symmetry, show that the coupling of the electric polarization and the strain leads to a first-order transition if the crystal is sufficiently ”soft” (i.e. the elastic coefficient is less than some critical value).

Solutions:

(a)

$$f = A(P_x^2 + P_y^2 + P_z^2) + B(P_x^4 + P_y^4 + P_z^4) + C(P_x^2 P_y^2 + P_y^2 P_z^2 + P_z^2 P_x^2)$$

where $A(T < T_c) < 0, B > 0, C \geq -B$ depend on pressure and temperature.

(b) By minimizing the free energy, we get

$$2AP_x + 4BP_x^3 + 2CP_x(P_Y^2 + P_z^2)$$

and two equations with permuted spatial indices. If all components of the polarization are non-zero, they must be equal and $f = -3A^2/4(B + c)$. If one is zero, the other two are equal and $f = -A^2/(2B + C)$. If two are zero, then $f = -A^2/4B$

The second case never appears, since is the free energy cannot be simultaneously smaller than both the first and the third case. For the first case to appear we need $= B < c < 2B$ and for the third $C > 2B$.

(c)

(d) Let’s assume distortion along the z-axis. $f_{strain} = \frac{2}{2}ks^2 + DsP_z^2$. If we add this to the terms in the free energy we had before and minimize, we get $f_s = -D^2P_z^4/2k$