TFY4245/FY8917 Solid State Physics, Advanced Course

Problemset 7

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SUGGESTED SOLUTION

Problem 1

(a) Consider a free energy F with an order parameter M which truncates the expansion at $g_n M^n$ where n is odd. This term will dominate when M becomes large. If g_n is positive, the free energy increases indefinitely when $M > 0$ and grows in magnitude. However, the free energy decreases indefinitely when $M < 0$ and grows in absolute value $|F|$. Vice versa for negative g_n. Thus, we see that regardless of the sign of g_n, the final odd term will lead to an unbound free energy from below, which is unphysical.

(b) We have

$$F = \frac{1}{2}g_2M^2 - \frac{1}{3}g_3M^3 + \frac{1}{4}g_4M^4. \tag{1}$$

Let us first consider the sign of the coefficients. We need $g_4 > 0$ for stability. The minus sign in front of g_3 does not cause loss of generality: if it was positive, just redefine $M' = -M$ to get a negative sign for the cubic term in a free energy $F = F(M')$. So we can set $g_3 > 0$. Finally, g_2 can be positive or negative, so we need to consider both cases.

The equilibrium condition is obtained from $dF/dM = 0$:

$$g_2M - g_3M^2 + g_4M^3 = 0. \tag{2}$$

One possible solution is $M = 0$. If $M \neq 0$, we have two other possible solutions:

$$M = M_\pm = \frac{g_3 \pm \sqrt{g_3^2 - 4g_2g_4}}{2g_4}. \tag{3}$$

These solutions can only give a real M if $g_3^2 - 4g_2g_4 > 0$: otherwise, the only solution is $M = 0$. So assume $g_3^2 > 4g_2g_4$ in order to not only face the trivial scenario of $M = 0$.

The question is now which solution that has the lowest free energy.

Case 1: $g_2 > 0$

Consider first the solution M_-. To determine if this corresponds to a minimum or a maximum, we check the sign of d^2F/dM^2 at $M = M_-$. This is evaluated as

$$\frac{d^2F}{dM^2} = \sqrt{g_3^2 - 4g_2g_4} - g_3. \tag{4}$$

If $g_2 > 0$, as assumed here, this is a maximum since then $d^2F/dM^2 < 0$. So we only need to consider M_+ as a contender for the ground-state in the present case, since M_- gives a (local) maximum in the free energy.

We proceed to compare $F(0)$ with $F(M_+)$. What is the condition for g_2, g_3, g_4 which makes these free energies equal? We have

$$F(M_+) = F(0) \to \frac{1}{2}g_2M_+^2 + \frac{1}{3}g_3M_+^3 + \frac{1}{4}g_4M_+^4 = 0. \tag{5}$$

Moreover, the stationary points of the free energy are given by $dF/dM = 0$, so that

$$g_2 - g_3M_+ + g_4M_+^2 = 0. \tag{6}$$

We then have to fulfil the following two quadratic equations simultaneously, after dividing Eq. (5) on M_+^2:

$$\begin{aligned} g_2 - g_3M_+ + g_4M_+^2 &= 0, \\ \frac{1}{2}g_2M_+^2 + \frac{1}{3}g_3M_+^3 + \frac{1}{4}g_4M_+^4 &= 0. \end{aligned} \tag{7}$$

Eliminating the quadratic term gives $M_+ = 3g_2/g_3$. Inserting now the general expression we found above for M_+ into this equation gives us the desired relation between g_2, g_4, g_6:

$$g_3^2 = \frac{9}{2}g_2g_4. \tag{8}$$

Once g_3 becomes larger than this value, $F(M_+)$ will take over the role as global minimum from $F(0)$.

Thus, we have found the following:

$$\begin{aligned} g_2 > \frac{g_3^2}{4g_4} &: 1 \text{ real root } M = 0 \\ \frac{g_3^2}{4g_4} > g_2 > \frac{2g_3^2}{9g_4} &: 3 \text{ real roots, minimum at } M = 0 \\ \frac{2g_3^2}{9g_4} > g_2 &: 3 \text{ real roots, minimum at } M = M_+ = \frac{g_3}{2g_4} + \sqrt{\left(\frac{g_3}{2g_4}\right)^2 - \frac{g_2}{g_4}} \end{aligned} \tag{9}$$

The solution $M = 0$ is the global minimum of the free energy for $g_2 > 0$ when $g_3 = 0$. As g_3 increases, one reaches a range $\frac{g_3^2}{4g_4} > g_2 > \frac{2g_3^2}{9g_4}$ where there is a global minimum at $M = 0$, a local minimum at $M = M_+$, and a local maximum at $M = M_-$ with $M_+ > M_- > 0$. As g_3 increases further, for $2g_3^2/9g_4 > g_2$ there is a local minimum at $M = 0$, a global minimum at $M = M_+$, and a local maximum at M_-, again with $M_+ > M_- > 0$. The same reasoning as above can also be applied if a finite g_3 exists in all cases and it is g_2 that gradually is reduced in magnitude.

Case 2: $g_2 < 0$
If $g_2 < 0$, we know that the solution $M = 0$ is a maximum since then $d^2F/dM^2 < 0$. However, the solution $M = M_-$ gives

$$\frac{d^2F}{dM^2} = \sqrt{g_3^2 - 4g_2g_4} - g_3. \tag{10}$$

which is now a minimum since $d^2F/dM^2 > 0$. Nevertheless, the solution $M = M_+$ remains a global minimum, as can be verified by comparing the magnitude of F at $M = M_\pm$. So for $g_2 < 0$, there is a local maximum at $M = 0$, a local minimum at $M = M_-$, and a global minimum at $M = M_+$ with $M_+ > 0 > M_-$.

In summary, with $g_3 = 0$ we have a second order transition at the temperature where $g_2 = 0$, as we have seen in the lectures. When adding g_3, there is a discontinuous (first order) transition at $g_2 = 2g_3^2/9g_4 > 0$ where the magnetization that provides the lowest free energy changes abruptly from $M = 0$ to $M_c = 2g_3/3g_4$. This occurs at a temperature before g_2 reaches the value $g_2 = 0$ where the curvature at $M = 0$ turns negative. Thus, if we write $g_2 = \alpha(T - T_0)$, then the expected second order transition at $T = T_0$ is preempted by a first order transition at $T_c = T_0 + 2g_3^2/9\alpha g_4$ as determined from the condition $g_3^2 = 9g_2g_4/2$. As g_2 becomes negative, the system remains in the ordered state with finite M.

Problem 2

The (relative) dielectric constant ε_r is generally defined as:

$$\varepsilon_r = 1 + \frac{P}{\varepsilon_0 E}. \tag{11}$$

Thus, we need to compute the ratio of P and E above T_c for the free energy provided in the problem text. The equilibrium polarization in an applied electric field E satisfies the extremum condition

$$\frac{dF}{dP} = 0 = -E + g_2P + g_4P^3. \tag{12}$$

Neglecting the P^4 term above T_c, we get $E = g_2P$ so that

$$\varepsilon(T > T_c) = 1 + \frac{1}{g_2\varepsilon_0}. \tag{13}$$

Note that the g_4-term contribution to P can be neglected safely when $E \neq 0$, whereas it clearly cannot for $E = 0$.