

Problem 1.

a) In second-order transitions, P increases monotonically from 0 at the phase transition, where the phases of the ordered and disordered state are in equilibrium.

=> Close to T_C , $G(P)$ is described mainly by the lower-order terms.

$g_0(T)$: In the disordered phase, $P = 0$ in absence of external electric fields. Thus, $G(T, P) = g_0(T) = G_2(T); T \geq T_C$, i.e $g_0(T)$ represents the free energy of the disordered phase for temperatures above T_C . It is a second order transition, so at T_C both $G_1(T) = G_2(T)$ and

$\frac{\partial G_1}{\partial T} = \frac{\partial G_2}{\partial T}$, thus over a small temperature region below T_C we may let

$$g_0(T) \approx g_0(T_C) = G_2(T_C) = G_1(T_C)$$

$g_1(T), g_3(T)$: A requirement to the ordered phase of second order phase transitions is $G(P) = G(-P)$, which may hold only if $g_1 = g_3 = 0$.

Thus, the free energy becomes

$$G(T, P) = g_0(T) + \frac{1}{2} g_2(T) P^2 + \frac{1}{4} g_4(T) P^4$$

System in equilibrium with respect to P at any T :

$$\frac{\partial G}{\partial P} = 0 = P(g_2(T) + g_4(T) P^2)$$

$$): P = 0 \quad \vee \quad P = \pm \sqrt{-\frac{g_2(T)}{g_4(T)}}$$

$g_4(T)$: with the given form for $g_2(T)$, restrictions are imposed on $g_4(T)$ from requiring the polar state to represent the free energy minimum below T_C :

2. $T > T_C$:

Here $g_0(T) = G_2(T)$, which may be regarded more or less constant for temperatures close to T_C .

We find: $g_2(T) = \gamma(T - T_C) > 0 \Rightarrow g_4 < 0$ gives real solution, while $g_4 > 0$ gives imaginary solution.

Energy minima:

$$i. P = 0 \Rightarrow G(T, P = 0) = g_0(T)$$

$$ii. \text{ For the real non-zero solution, } G(T, P) = g_0(T) + \frac{g_2(T)^2}{4|g_4(T)|} > g_0(T)$$

Thus the free energy minimum is $G(T, P=0) = g_0(T) = G_2(T)$, favouring a non-polar state.

1. $T < T_C$:

$g_2 = \gamma(T-T_C) < 0 < 0 \Rightarrow \underline{g_4 > 0 \text{ gives real solution}}$, while $g_4 < 0$ gives imaginary solution.

Energy minima:

i. $P = 0 \Rightarrow G(T, P = 0) = g_0(T) \approx g_0(T_C) = G_2(T_C)$

ii. For the real non-zero solution, $G(T, P) = g_0(T_C) - \frac{g_2(T)^2}{4g_4(T)} < g_0(T_C)$

Thus, the polar state with $P = \pm \sqrt{-\frac{g_2(T)}{g_4(T)}}$ gives energy minima below T_C , and accordingly g_4 must be restricted such that $g_4(T) > 0$ for all $T < T_C$.

As shown under points 1 and 2 above, $G(T, P)$ in the Landau expansion form gives a satisfactory description of the free energy of the second-order para- $\rightarrow$ ferroelectric phase transition, and defines the correct polar properties for the stable state above and below T_C .

b) With the external field present, the Gibbs free energy becomes

$$G(T, P, E_{ext}) = G(T, P) - \vec{E}_{ext} \vec{P} = g_0(T) + \frac{1}{2} g_2(T) P^2 + \frac{1}{4} g_4(T) P^4 - \vec{E}_{ext} \vec{P}$$

where the vectors can be replaced by scalars when the external field is considered to be aligned parallel or antiparallel with the ordering parameter.

Comparing with the zero-field situation from a).
System in thermal equilibrium at any temperature,

$$\frac{\partial G}{\partial P} = g_4 P^3 + g_2 P \mp E_{ext} = 0$$

Thus, with a non-zero external field present, the equilibrium polarisation magnitudes associated with energy minimisation are solutions satisfying the third order eqn. above, and accordingly they change with the magnitude of the field. For temperatures above T_C , and with a non-zero E , clearly the net polarisation attains non-zero values if the system has any dielectric response (ionic, orientation dependent, electronic). Normally, however, in ferroelectrics the paraelectric response above T_C is weak, so that the P^3 becomes negligible, resulting in a susceptibility of the Curie-Weiss type, i.e. $\chi \approx \frac{C}{T-T_C}$. As $T < T_C$ and into the ferroelectric domain, however, P may rise spontaneously to attain values well above 0, accommodating to the presence of an external field. The 3rd order term cannot be neglected, and the equilibrium polarisation must be found from solutions of the 3rd order eqn.

For a linear system, the dielectric susceptibility

$$\frac{\partial G}{\partial P} = 0 = \mp E_{ext} + g_2 P + g_4 P^3$$

$$): E_{ext} = \pm(g_2 P + g_4 P^3)$$

$$\chi = \left[\frac{dE_{ext}}{dP} \right]_{E_{ext}=E}^{-1} = (g_2 + 3g_4 P_E^2)^{-1}$$

where P_E is the equilibrium value of the order parameter in an external field $E_{ext}=E$.

When $E=0$, eqn (*) returns to the situation in a) for which we already found solutions.

$T \geq T_C$:

$$P_0=0 \Rightarrow \chi = 1/g_2 = \frac{1}{\gamma(T-T_C)}$$

$T < T_C$:

$$P_0 = \pm \sqrt{-\frac{g_2}{g_4}} \Rightarrow \chi = \frac{1}{g_2 + 3g_4 \left(\frac{-g_2}{g_4} \right)} = \frac{1}{-2g_2} = \frac{1}{2\gamma(T_C - T)}$$

c) The polarisation associated with ion displacements may be expressed $P = \sum_i n_i q_i \Delta r_i$ where the sum is taken over the individual ions that contribute.

From figure 1 we find that $n_{Ba^{2+}} = 8 \cdot 1/8/V = 1/a^3 = n_{Ti^{4+}}$ and from the text we are told that $\Delta r_{Ba^{2+}} = \Delta r_{Ti^{4+}} = \Delta r$, so we have

$$\Delta r(T) = \frac{P(T)a^3}{q_{Ba^{2+}} + q_{Ti^{4+}}} = \frac{P(T)a^3}{6e}$$

Entering the polarisation values given, we find: $\Delta r(392K) = 0.03 \text{ \AA}$; $\Delta r(300K) = 0.18 \text{ \AA}$

We have identical shifts for the positive ions, and consider these to account for the full polarizability of $BaTiO_3$.

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\chi}{\chi + 3} = \frac{\alpha_{BTO}}{3a^3 \epsilon_0} \Rightarrow \alpha_{BTO} = 3\epsilon_0 a^3 \frac{\chi}{\chi + 3}$$

Close to T_C we may employ the susceptibilities from b), i.e.:

$T \geq T_C :$

$$\alpha_{BTO} = 3\epsilon_0 a^3 \frac{\frac{1}{\gamma(T-T_C)}}{\frac{1+3\gamma(T-T_C)}{\gamma(T-T_C)}} = \frac{3\epsilon_0 a^3}{1+3\gamma(T-T_C)}$$

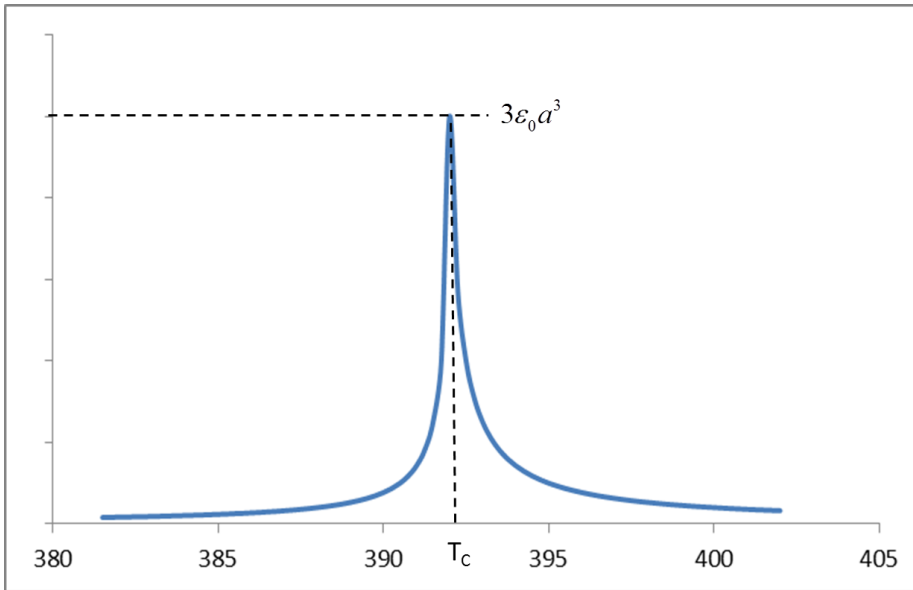
$T < T_C :$

$$\alpha_{BTO} = 3\epsilon_0 a^3 \frac{\frac{1}{2\gamma(T_C-T)}}{\frac{1+6\gamma(T_C-T)}{2\gamma(T_C-T)}} = \frac{3\epsilon_0 a^3}{1+6\gamma(T_C-T)}$$

So,

$$\alpha_{BTO}(T) = \begin{cases} \frac{3\epsilon_0 a^3}{1+3\gamma(T-T_C)}, & T \geq T_C \\ \frac{3\epsilon_0 a^3}{1+6\gamma(T_C-T)}, & T < T_C \end{cases}$$

Sketch



$\alpha_{BTO}(T)$ rises anomalously in the proximity of T_C , and shows archetypical behaviour for a critical parameter in a second order transition. In second order displacive transitions, the spontaneous polarisation caused by ion displacements at or about T_C is related to a T.O. phonon softening via the LST relation. From the result it can be seen directly that the polarizability, and hence the static dielectric function, grows anomalously about T_C , such that T_C represents a critical point. From the LST relation this implies that $\omega_{TO} \xrightarrow{T \rightarrow T_C} 0$ from both sides, which allows for the lattice to polarise

spontaneously at T_C even without an external field present. As T moves away from the critical point, the T.O. phonon softening vanishes and the T.O. lattice restoring forces regain their strengths.

Returning to the Classius Mosotti relation

$$\begin{aligned}
\frac{\chi}{\chi+3} &= \frac{\alpha_{BTO}(T)}{3a^3\epsilon_0} \Rightarrow \chi\left(1 - \frac{\alpha_{BTO}(T)}{3a^3\epsilon_0}\right) = \frac{\alpha_{BTO}(T)}{a^3\epsilon_0} \\
\Rightarrow \chi &= \frac{1}{2\gamma(T_c - T)} = \frac{\frac{\alpha_{BTO}(T)}{a^3\epsilon_0}}{1 - \frac{\alpha_{BTO}(T)}{3a^3\epsilon_0}} \\
\Rightarrow \gamma &= \frac{1 - \frac{\alpha_{BTO}(T)}{3a^3\epsilon_0}}{2 \frac{\alpha_{BTO}(T)}{a^3\epsilon_0} (T_c - T)}
\end{aligned}$$

From the previous solution we found $\alpha_{BTO}(T_c) = 3\epsilon_0 a^3$, so from the measurement done 0.5 K into the ferroelectric phase region, we find

$$\gamma = \frac{1 - 1/2}{3(1/2)K} = \frac{1}{3} K^{-1}$$

Problem 2

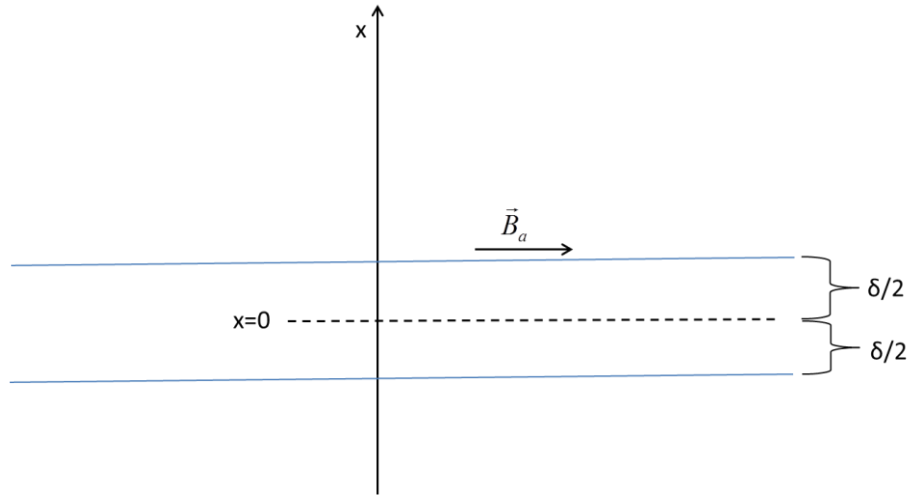
- a) From Maxwell, $\nabla \times \vec{B} = \mu_0 \left(\vec{j} + \frac{\partial \vec{D}}{\partial t} + \nabla \times \vec{M} \right) = \mu_0 \vec{j}$, assuming no displacement currents or Amperian currents/magnetisation currents.

Take the curl once more, and introduce the superconducting current density

$$\begin{aligned}
\nabla \times \nabla \times \vec{B} &= \nabla \cdot (\nabla \cdot \vec{B}) - \nabla^2 \vec{B} = -\nabla^2 \vec{B} = \mu_0 (\nabla \times \vec{j}) \\
&= -\mu_0 \frac{e}{m_e} n_{c.p.} (\hbar \nabla \times \nabla \theta(r) + 2e \nabla \times \vec{A}) = -\mu_0 \frac{2e^2 n_{c.p.}}{m_e} \vec{B} \\
\Rightarrow \nabla^2 \vec{B} &= \frac{2e^2 \mu_0 n_{c.p.}}{m_e} \vec{B} = \lambda_L^{-2} \vec{B}
\end{aligned}$$

The physical interpretation of λ_L is that it reflects the penetration depth of the magnetic field into the current-transporting media. In a superconductor the length is referred to as the London penetration depth and corresponds to a surface near region where the Meissner effect is only partial, and also the region in which the superconductive current is flowing. The equation for the superconductive current density is identical.

b)



From the London eqn., $\frac{d^2 B}{dx^2} = \frac{B}{\lambda_L^2} \Rightarrow B(x) = C_1 e^{x/\lambda_L} + C_2 e^{-x/\lambda_L}$ as solutions at both sides of the plate.

The external magnetic field is the same at both sides of the plate. Demanding continuity at the boundaries,

$$B(\pm \frac{\delta}{2}) = B_a \Rightarrow C_1 = C_2 = C$$

$$\Rightarrow B_a = C(e^{-\delta/2\lambda_L} + e^{\delta/2\lambda_L})$$

$$\Rightarrow C = \frac{B_a}{e^{-\delta/2\lambda_L} + e^{\delta/2\lambda_L}}$$

Accordingly,

$$B(x) = B_a \frac{e^{-x/\lambda_L} + e^{x/\lambda_L}}{e^{-\delta/2\lambda_L} + e^{\delta/2\lambda_L}} = B_a \frac{\cosh(x/\lambda_L)}{\cosh(\delta/2\lambda_L)}$$

The magnetisation inside the plate:

$$\vec{B}(x) = \mu_0(\vec{M}(x) + \vec{H}_{ext}) \Rightarrow M(x) = \frac{1}{\mu_0}(B(x) - B_a) = \frac{B_a}{\mu_0} \left(\frac{\cosh(x/\lambda_L)}{\cosh(\delta/2\lambda_L)} - 1 \right)$$

Let $\delta \ll \lambda_L$, so that $|x| \leq \delta/2$ (even smaller) inside the plate/thin film, and expand the hyperbolic functions (2nd order is adequate when the arguments are small):

$$M(x) = \frac{B_a}{\mu_0} \left(\frac{1 + \frac{x^2}{2\lambda_L^2} - 1 - \frac{\delta^2}{8\lambda_L^2}}{1 + \frac{\delta^2}{8\lambda_L^2}} + O^{(4)} + \dots \right) \approx \frac{B_a}{\mu_0} \left(\frac{4x^2 - \delta^2}{8\lambda_L^2 + \delta^2} \right) \approx \frac{B_a}{8\lambda_L^2 \mu_0} (4x^2 - \delta^2)$$

c) The magnetic field contribution to the free energy density is

$$dF_{s.c.} = dW = -\mu_0 M dH = -M dB_a$$

So accordingly,

$$\begin{aligned} F_{s.c.}(0, x, B_a) &= F_{s.c.}(0) - \frac{1}{8\mu_0\lambda_l} (4x^2 - \delta^2) \int_0^{B_a} B_a dB_a \\ &= F_{s.c.}(0) + \frac{B_a^2}{16\mu_0\lambda_l} (\delta^2 - 4x^2) \end{aligned}$$

The average magnetic contribution to F inside the film is:

$$\langle F(B_a) \rangle_x = \frac{B_a^2}{16\mu_0\lambda_l^2} \frac{\int_0^{\delta/2} (\delta^2 - 4x^2) dx}{\int_0^{\delta/2} dx} = \frac{2B_a^2}{16\mu_0\lambda_l^2} \delta \left(\frac{\delta^3}{2} - \frac{1}{3} \frac{\delta^3}{2} \right) = \frac{B_a^2}{16\mu_0\lambda_l^2} \frac{2}{3} \delta^2 = \frac{B_a^2}{24\mu_0} \left(\frac{\delta}{\lambda_l} \right)^2$$

For a bulk superconductor the critical field is defined by the magnetic field energy superseding the stabilisation energy of the superconductor. Thus,

$$F_b = F_{s.c.}(0) + \frac{1}{2\mu_0} H_c^2 \approx F_{s.c.}(0) + \frac{B_{ac}^2}{24\mu_0} \left(\frac{\delta}{\lambda} \right)^2$$

where B_{ac} is the critical field of the thin film. We find:

$$\frac{1}{2\mu_0} H_c^2 \approx \frac{B_{ac}^2}{24\mu_0} \left(\frac{\delta}{\lambda} \right)^2 \Rightarrow B_{ac} = \sqrt{12} H_c \left(\frac{\lambda}{\delta} \right)$$

implying that the thin film stability to external fields is higher than for the bulk superconductor.

For a 2D superconductor modelled as a very thin sheet, the minimum size required to form a superconducting region (=coherence length) may still be satisfied by cooper pairs separated in the yz-plane. Considering the current density, however, we may run into problems. This should also be given by the London eqn., but taking into account the direction of B inside the film, the current needs to reflect loops with one component along x, implying that x need to have a finite size for the current to run.

3 a) Weak magnetisation in the paramagnetic phase, so we may apply Curies law:

$$\chi = \frac{\partial M}{\partial H} \approx \frac{M}{H} = \frac{C}{T}$$

The magnetisation is given by

$$\text{A-site lattice: } M_A T = CH_A = C(H_{ext} - \lambda M_B - \nu M_A)$$

$$\text{B-site lattice: } M_B T = CH_B = C(H_{ext} - \lambda M_A - \nu M_B)$$

At $T = T_N$ the system should undergo spontaneous magnetisation, even in the absence of external fields. Thus:

$$\begin{aligned} \begin{vmatrix} T + \nu C & \lambda C \\ \lambda C & T + \nu C \end{vmatrix} &= (T + \nu C)^2 - \lambda^2 C^2 = 0 \\ \Rightarrow \pm(T + \nu C) &= \pm \lambda C, \quad \lambda C > 0; T_N > 0 \\ \Rightarrow T_N &= C(\lambda - \nu) \end{aligned}$$

To find the paramagnetic susceptibility of the total system, first express the total magnetisation of the two connected sublattices:

$$\begin{aligned} MT &= (M_A + M_B)T = 2CH_{ext} - C(\lambda + \nu)M \\ \Rightarrow M &= \frac{2CH_{ext}}{T + (\lambda + \nu)C} \end{aligned}$$

Thus,

$$\chi = \frac{\partial M}{\partial H} = \frac{2C}{T + C(\lambda + \nu)} = \frac{2C}{T + \theta}, \quad \text{where } \theta = \frac{(\lambda + \nu)}{(\lambda - \nu)} T_N$$

3 b) Below the transition temperature, the two sublattices spontaneously order into two antiparallel systems, $M_A = -M_B$, so

$$H_A = -\lambda M_B - \nu M_A = (\lambda - \nu)M_A; \quad H_B = (\lambda - \nu)M_B$$

Accordingly we should use the Curie-Brillouin law, which gives us

$$\begin{aligned} M_A &= \frac{1}{2} \frac{N}{V} \cdot g(JLS) J \mu_B \cdot B_J \left(\frac{g(JLS) J \mu_B \mu_0 (\lambda - \nu) M_A}{k_B T} \right) \\ M_B &= \frac{1}{2} \frac{N}{V} \cdot g(JLS) J \mu_B \cdot B_J \left(\frac{g(JLS) J \mu_B \mu_0 (\lambda - \nu) M_B}{k_B T} \right) \end{aligned}$$

The $\frac{1}{2}$ prefactor enters since the N atoms are parted into two antiparallel spin systems.

$J=1/2$:

$$B_J(x) = 2 \coth(2x) - \coth(x) = \frac{2(\coth^2 x + 1)}{2 \coth x} - \frac{2 \coth^2 x}{2 \coth x} = \frac{1}{\coth x} = \tanh x$$

$$g(JLS) = \frac{3}{2} + \frac{1}{2} = 2$$

Hence

$$M_A = \frac{1}{2} n \mu_B \cdot \tanh \left(\frac{\mu_B \mu_0 (\lambda - \nu) M_A}{k_B T} \right)$$

$$M_B = \frac{1}{2} n \mu_B \cdot \tanh \left(\frac{\mu_B \mu_0 (\lambda - \nu) M_B}{k_B T} \right)$$

To find the Neel-temperature, we select one of the two sublattice systems, and let $T \rightarrow T_N$ from below. At the second order transition temperature, and in the absence of external fields, the magnetisation of each subsystem will be weak, so

For small x $\tanh x \approx x \Rightarrow$

$$M_A(T_N) \approx \frac{n \mu_B^2 \mu_0 (\lambda - \nu) M_A(T_N)}{2 k_B T_N} \Rightarrow T_N = \frac{n \mu_B^2 \mu_0 (\lambda - \nu)}{2 k_B}$$

Low-T convergence:

Set:

$$x = \frac{\mu_B \mu_0 (\lambda - \nu) M}{k_B T} \Rightarrow M = \frac{1}{2} n \mu_B \tanh(x)$$

$$\frac{M}{\frac{1}{2} n \mu_B} = \frac{M}{M_S} = \frac{T}{T_N} x \Rightarrow \frac{T}{T_N} x = \frac{M}{M_S} = \tanh x \quad \vee \quad x = \frac{T_N}{T} \frac{M}{M_S} \approx \frac{T_N}{T}$$

$$\Rightarrow M \approx M_S (1 - 2e^{-2T_N/T})$$

A spin wave approach to the temperature dependence of M gives rise to the so-called Bloch $T^{3/2}$ law, whereas the mean field approach suggests an exponential T-dependency. The Bloch $T^{3/2}$ law has been found to fit well with low temperature experimental results.

In reality neither will give an accurate description of the low temperature trend for the antiferromagnet. The mean field approach has its already mentioned deviating trend at low T for both spin systems, and the Bloch $T^{3/2}$ -law is derived for a single parallel spin system with n.n. exchange only, not two exchanging antiparallel systems. It is therefore likely that the antiferromagnet require a more complicated spin wave based model.