

5FoP3B Part II Lecture 12: Ginzburg-Landau theory of Ferroelectrics

Ferroelectrics are characterised by a **spontaneous polarisation** P_s even in the absence of an electric field. An example is BaTiO_3 where the polarisation is due to a small displacement of negatively charged oxygen ions w.r.t positively charged Ti ions. Ferroelectrics share similar properties to **ferromagnets**, such as **domains** and **hysteresis loops**. Another common feature is the **Curie temperature** T_c ; this is the temperature above which the ferroelectric transitions to the **paraelectric state** (cf. ferromagnetism-paramagnetism transition). *In the paraelectric state there is no spontaneous polarisation; it is favoured at high temperature due to the amplitude of thermal vibration being large compared to the ion displacements causing polarisation.* Two forms of phase transition are observed: (i) a transition where P_s decreases continuously to zero at T_c (Figure 1a) and (ii) a transition where P_s changes discontinuously at T_c (Figure 1b). *If we take polarisation as a measure of order and therefore entropy the first example corresponds to a **second order transition**, since there is no change in the entropy at T_c . In other words no **latent heat** is involved.* On the other hand the second example is a **first order transition** (i.e. discontinuous change in entropy or non-zero latent heat). *Another interesting feature of the ferroelectric to paraelectric transition is that the **dielectric constant** ϵ_r is extremely large close to the Curie temperature (Figure 1c).*

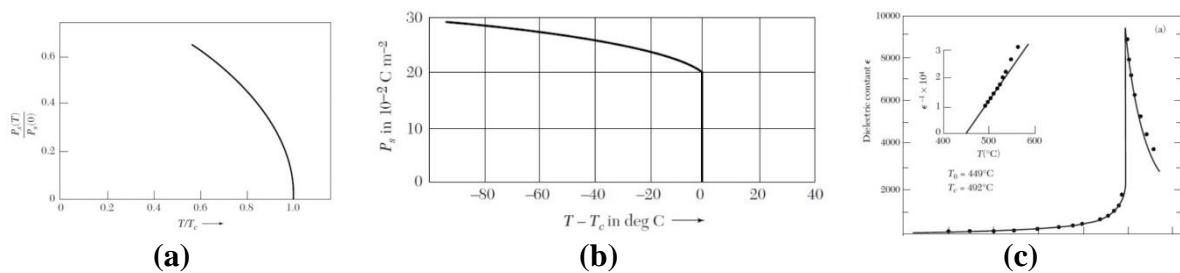


Fig. 1: Spontaneous polarisation as a function of temp for (a) second order and (b) first order transition. (c) shows ϵ_r as a function of temp (the ‘spike’ in ϵ_r occurs at T_c).

Ginzburg-Landau (GL) theory: second order transitions

GL is a *phenomenological* theory which expresses the free energy as a function of a characteristic order parameter (e.g. $|\psi|^2$ or Cooper pair density for superconductivity). For ferroelectricity the order parameter is the polarisation P . The free energy $G_{FE}(T)$ of the ferroelectric phase at temperature T is given by:

$$G_{FE}(T) = G_{PE}(T) + \frac{1}{2}g_2P^2 + \frac{1}{4}g_4P^4 \quad \dots (1)$$

where $G_{PE}(T)$ is the free energy of the paraelectric phase and g_2, g_4 are coefficients in the expansion which may also be functions of temperature. Equation (1) is valid close to the Curie temperature T_c and contains only even powers of P , since G_{FE} must be independent of the polarisation direction (i.e. its sign). Furthermore, the G_{FE} vs P^2 curve must have a minimum in order to form an equilibrium ferroelectric phase. Since Equation (1) is quadratic in P^2 this means that $g_4 > 0$. To determine the spontaneous polarisation of the ferroelectric phase we calculate the turning point by setting $(\partial G_{FE}/\partial P) = 0$, i.e.

$$\frac{\partial G_{FE}}{\partial P} = P(g_2 + g_4 P^2) = 0 \quad \dots (2)$$

Equation (2) has solutions $P = 0$ and $P = \sqrt{-\frac{g_2}{g_4}}$. Consider the latter solution. For $T < T_c$ the ferroelectric phase is stable, so that in order to have a non-zero P the value of g_2 must be negative, i.e. $g_2(T < T_c) < 0$. At $T = T_c$, $P = 0$ for a second order transition, and therefore $g_2(T_c) = 0$. Above T_c the paraelectric phase is stable, so that only the first solution $P = 0$ is valid, and $P = \sqrt{-\frac{g_2}{g_4}}$ must give a non-physical solution. This can happen if $g_2(T > T_c) > 0$.

From this an expression can be derived for g_2 using a Taylor series expansion, i.e.

$$f(x) = f(x_o) + f'(x_o)(x - x_o) + \frac{f''(x_o)}{2!}(x - x_o)^2 + \dots \quad \dots (3)$$

We substitute g_2 for f , T for x and T_o for x_o . To first order in ' x ' we find that:

$$g_2 = \gamma(T - T_o) \quad \dots (4)$$

where γ , T_o are positive constants and $T_o = T_c$ ¹. Equation (4) satisfies the conditions we deduced for g_2 using physical arguments. For g_4 we retain only the first term in the Taylor expansion (Equation 3), so that it is effectively a constant independent of temperature.

Substituting Equation (4) in $P = \sqrt{-\frac{g_2}{g_4}}$ we obtain an expression for the spontaneous polarisation (P_s):

$$P_s = \sqrt{\frac{\gamma(T_o - T)}{g_4}} = \sqrt{\frac{\gamma(T_c - T)}{g_4}} \quad \dots (5)$$

The P_s vs T curve predicted by Equation (5) agrees with experiment (Figure 1a). The (G_{FE} - G_{PE}) free energy curves at different temperature are shown schematically in Figure 2a.

¹ g_2 is written in this way, rather than $\gamma(T-T_c)$, since the same expression is used for first order transitions as well. However, for a first order transition $T_o \neq T_c$.

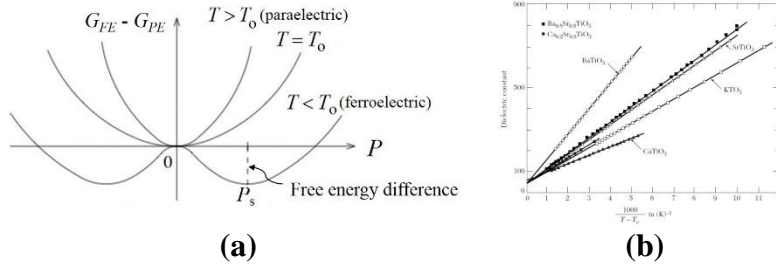


Fig. 2: (a) $(G_{FE} - G_{PE})$ vs. P curves. The minimum below $T_o = T_c$ gives P_s and free energy difference between ferroelectric and paraelectric phases. (b) ϵ_r vs $(T - T_c)^{-1}$ for several different dielectrics.

Consider now applying an electric field E . The free energy (Equation 1) is modified to:

$$G_{FE}(T) = G_{PE}(T) - EP + \frac{1}{2}g_2P^2 + \frac{1}{4}g_4P^4 \quad \dots (6)$$

The additional energy term $-EP$ is derived from the potential energy of an electric dipole moment μ in an electric field \mathbf{E} (i.e. potential energy = $-\mu \cdot \mathbf{E}$, which has a minimum when μ is parallel to \mathbf{E}). From $(\partial G_{FE} / \partial P) = 0$ the equilibrium polarisation at a given temperature is:

$$E = g_2P + g_4P^3 \quad \dots (7)$$

Let us examine the temperature range just above $T_o = T_c$ where the material is in the paraelectric phase and the polarisation is small under small applied electric fields. Since $P \approx 0$ we can ignore the P^3 term in Equation (7). Hence:

$$\frac{P}{E} = \frac{1}{g_2} = \frac{1}{\gamma(T - T_o)} = \frac{1}{\gamma(T - T_c)} \quad \dots (8)$$

From the definition of the electric displacement field, $\mathbf{D} = \epsilon_o \mathbf{E} + \mathbf{P} = \epsilon_o \epsilon_r \mathbf{E}$, it then follows that:

$$\epsilon_r = 1 + \frac{1}{\epsilon_o} \left(\frac{P}{E} \right) = 1 + \frac{1}{\gamma \epsilon_o (T - T_c)} \quad \dots (9)$$

Ginzburg-Landau therefore predicts the rapid increase in ϵ_r close to T_c (Figure 1c). This relationship has been experimentally verified on a number of dielectrics (Figure 2b).

Ginzburg-Landau (GL) theory: first order transitions

GL theory can be expanded to analyse first order transitions (Figure 1b) as well. However, the free energy expansion now contains a P^6 higher order term (cf. Equation 1):

$$G_{FE}(T) = G_{PE}(T) + \frac{1}{2}g_2P^2 + \frac{1}{4}g_4P^4 + \frac{1}{6}g_6P^6 \quad \dots (10)$$

Equation (10) is cubic in P^2 so that for a minimum it is required that $g_6 > 0$. Furthermore, we set g_4 *negative*, i.e. $g_4 = -|g_4|$, and $g_2 = \gamma(T - T_o)$, where γ and T_o are positive constants. Unlike second order transitions T_o here is **not** the Curie temperature (in fact it can be shown that $T_o < T_c$). The spontaneous polarisation P_s is given by the turning points ($\partial G_{FE}/\partial P = 0$):

$$\frac{\partial G_{FE}}{\partial P} = P(g_2 + g_4 P^2 + g_6 P^4) = 0 \quad \dots (11)$$

The solutions for (11) are $P_s = 0$ and from the quadratic in P^2 :

$$P_s^2 = \frac{-g_4 \pm \sqrt{g_4^2 - 4g_2g_6}}{2g_6} \quad \dots (12)$$

P_s for the ferroelectric phase corresponds to the non-zero solution to Equation (12) that gives a minimum in the free energy curve. This is illustrated in Figure 3. Below T_c the ferroelectric phase, as determined by the minimum, has lower energy than the paraelectric phase at $P = 0$ and is therefore the stable phase. As the temperature is increased P_s for the ferroelectric phase continuously decreases. However, at the Curie temperature T_c , the ferroelectric phase P_s is still non-zero and the free energies of both paraelectric and ferroelectric phases are equal (Figure 3). At temperature above T_c Equation (12) does not give a minimum and so the stable phase is the paraelectric phase at $P = 0$. The polarisation has therefore changed abruptly at T_c , as required for first order transitions (Figure 1b).

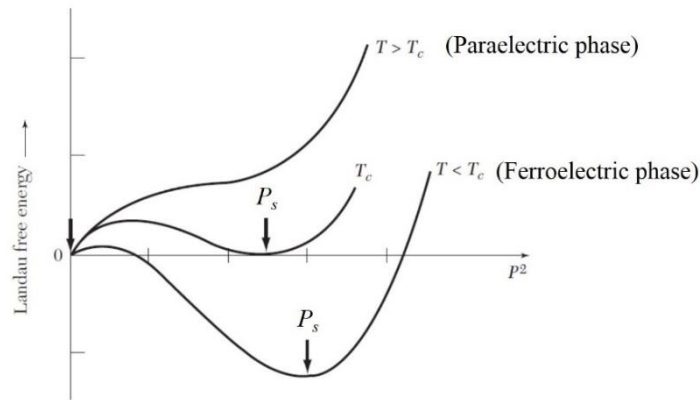


Figure 3: ($G_{FE} - G_{PE}$) vs P^2 curves at different temperatures. Below T_c the ferroelectric phase is stable with spontaneous polarisation P_s . At T_c both paraelectric ($P = 0$) and ferroelectric phases have equal energy, although P_s is still non-zero. Above T_c only the paraelectric phase is stable. The free energy of the paraelectric state is arbitrarily set to zero.