FoP 3B Part II

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Room 151

Lecture 12: Ginzburg-Landau theory of ferroelectrics

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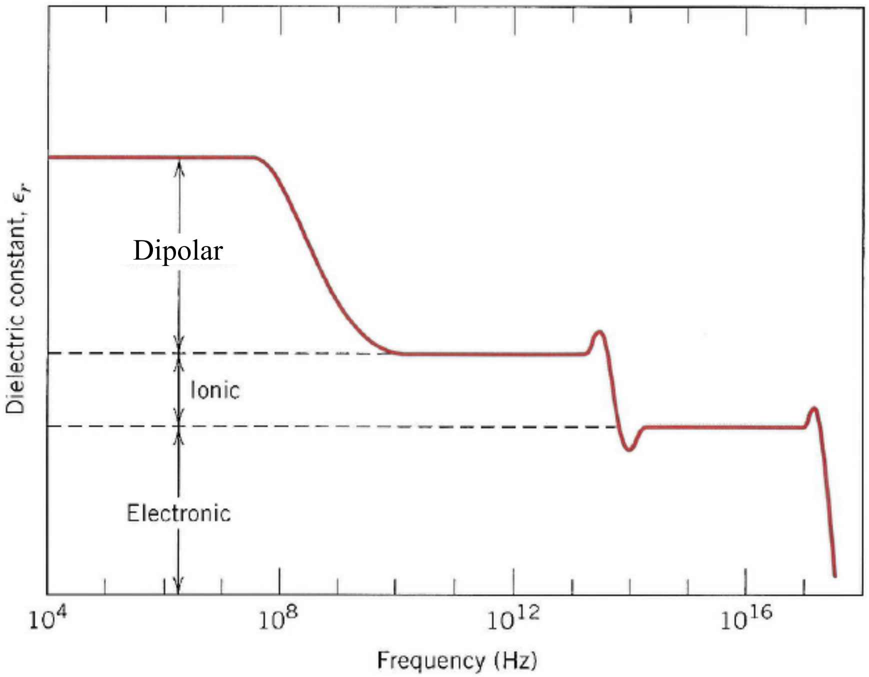
Summary of lecture 13

Polarisation mechanisms:

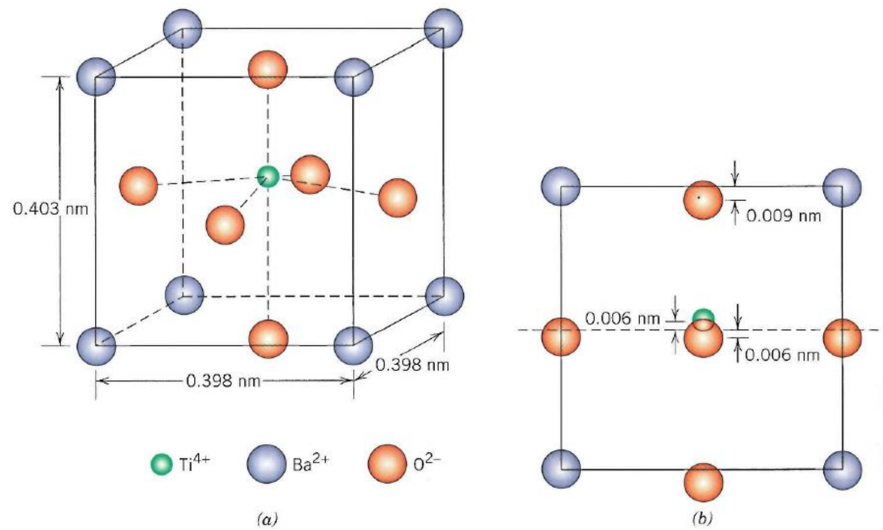


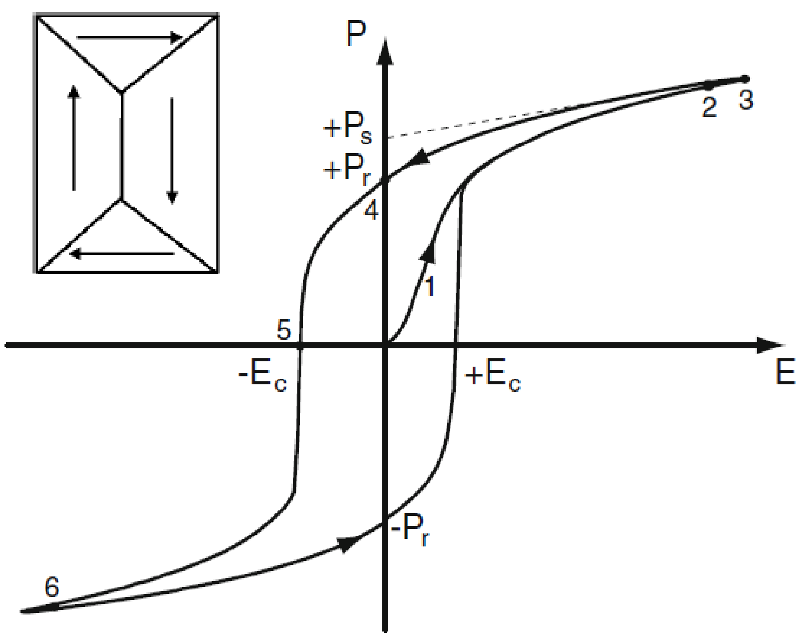
Electronic polarisation:

$$\alpha(\omega) = \frac{e^2}{m(\omega_o^2 - \omega^2)}$$

Electrons in atoms treated as harmonic oscillators

Ferroelectric crystals:





Aim of today's lecture

► Develop Ginzburg-Landau theory of ferroelectric crystals

Key concepts:

-Ferroelectric to paraelectric transition
-Dielectric function close to transition temperature
-First order and second order transitions

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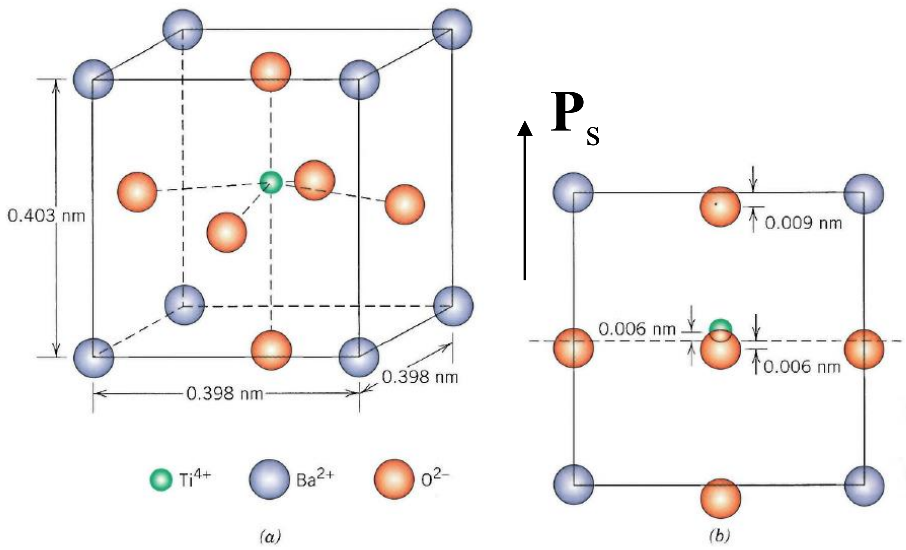
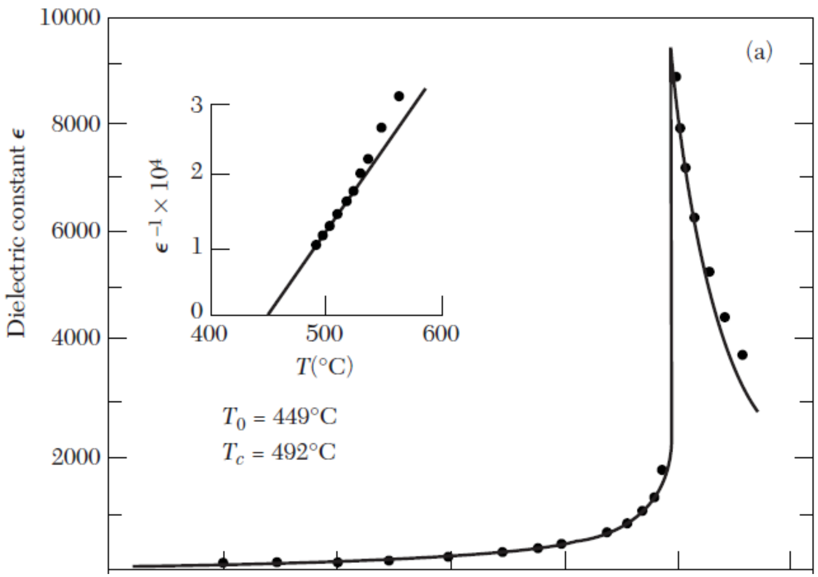
Ferroelectric to paraelectric transition





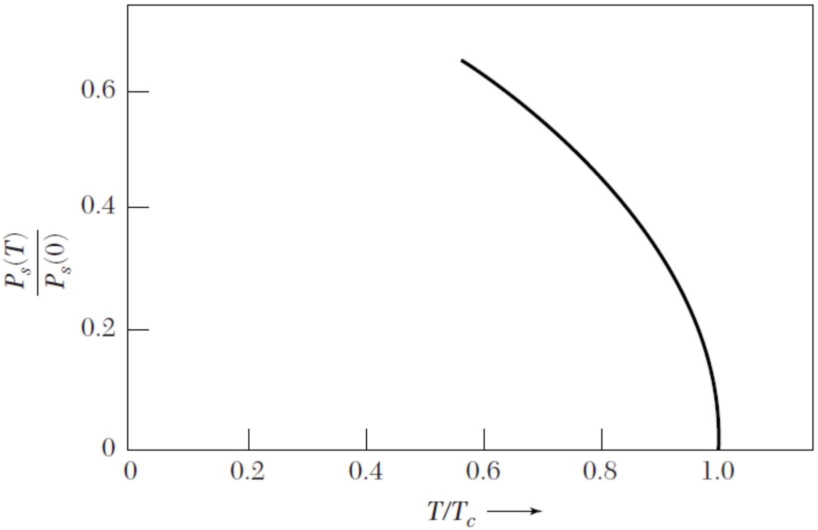
Above: Dielectric constant for $PbTiO_3$

-Relative shift of positive and negative ions destroyed at high temperatures.

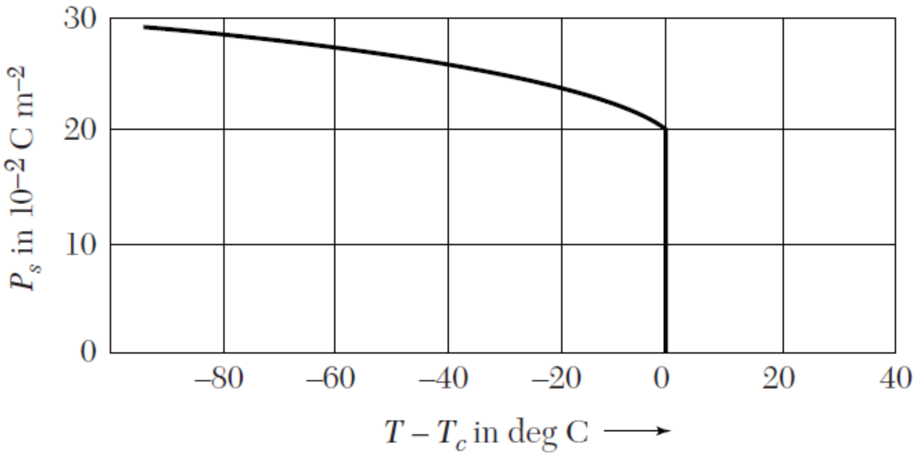
-Material converts to *paraelectric* state at the *Curie temperature*, with almost zero polarisation.

-Large increase in dielectric constant at transition temperature.

Polarisation change at transition temperature



Second order transition (e.g. $LiTaO_3$)



First order transition (e.g. $BaTiO_3$)

-Spontaneous polarisation ($\mathbf{P}_s$) is an order parameter in ferroelectrics (cf. Cooper pairs in superconductors or spontaneous magnetisation $\mathbf{M}_s$ in ferromagnets).

-Continuous decrease of $\mathbf{P}_s$ to zero (paraelectric state) for second order transformation. Discontinuous change in $\mathbf{P}_s$ for first order transformation.

Ginzburg-Landau theory (second order transitions)

For zero electric field conditions:

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

Free energy ferroelectric state

Free energy paraelectric state

- Free energy dependent only on even powers of polarisation P, since must be invariant on reversal of polarisation direction.

- For energy minimum require $g_4 > 0$.

- $g_2 = \gamma(T - T_o)$, where $\gamma > 0$ and T_o is a positive constant (NB: T_o is equal to the Curie temperature only for second order transitions)

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Spontaneous polarisation (second order transitions)

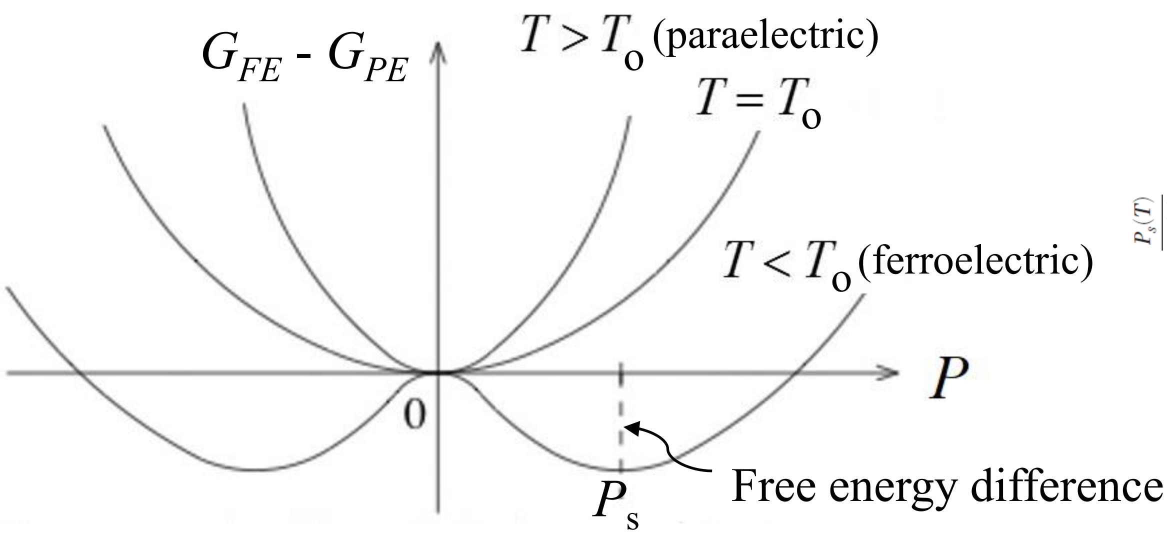
To determine spontaneous polarisation minimise G_{FE} w.r.t P:

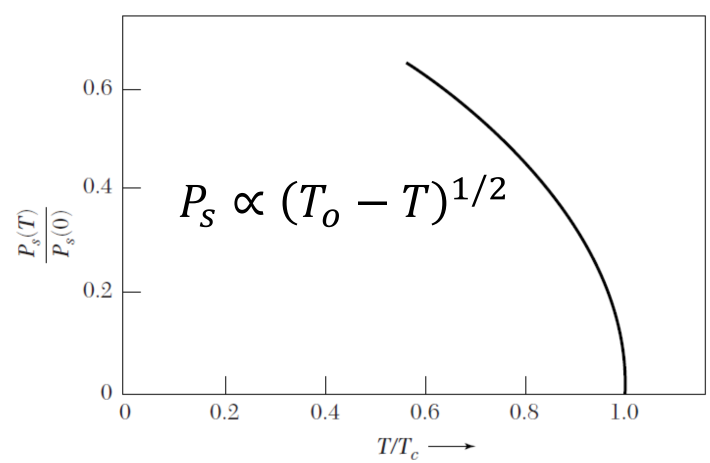
$$P(g_2 + g_4 P^2) = 0$$

Two possible solutions:

$$\text{(i)}\ \ P_s = 0 \qquad\qquad \text{(ii)}\ \ P_s = \left(-\frac{g_2}{g_4}\right)^{1/2} = \left(\frac{\gamma}{g_4}\right)^{1/2} (T_o - T)^{1/2}$$

Solution (ii) only valid for $T < T_o$. Above T_o only solution (i) exists (i.e. paraelectric state). T_o is therefore the Curie temperature.





Effect of applied field (second order transitions)

In the presence of an applied electric field (E):

$$G_{FE}(T) = G_{PE}(T) - EP + \frac{1}{2} g_2 P^2 + \frac{1}{4} g_4 P^4$$

Dipole potential energy

Minimising free energy:

$$E = g_2 P + g_4 P^3$$

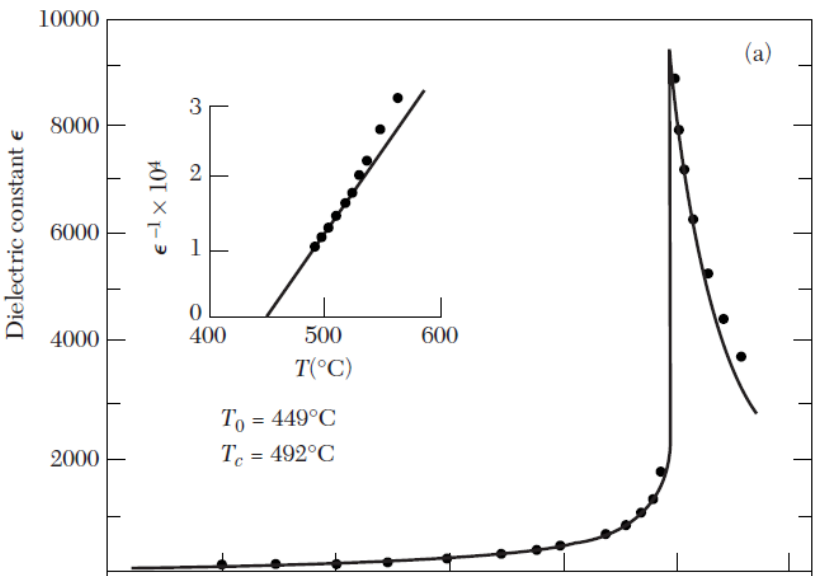
Above the Curie temperature $P \approx 0$. Therefore:

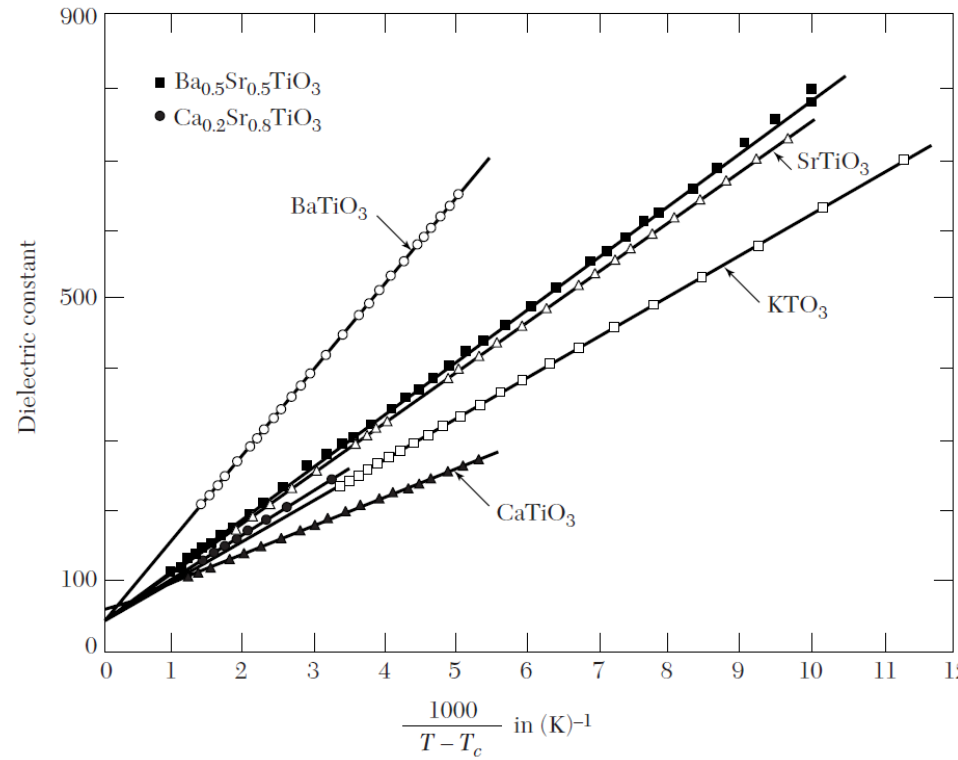
$$\frac{P}{E} = \frac{1}{g_2} = \frac{1}{\gamma(T - T_o)}$$

From $D = \epsilon_o E + P = \epsilon_o \epsilon_r E$, we have:

$$\epsilon_r = 1 + \frac{1}{\epsilon_o}\left(\frac{P}{E}\right) = 1 + \frac{1}{\gamma \epsilon_o (T - T_o)}$$

Dielectric constant





$$\epsilon_r = 1 + \frac{1}{\gamma \epsilon_o (T - T_o)}$$

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Ginzburg-Landau theory (*first* order transitions)

For zero electric field conditions:

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

Additional higher order term

- For energy minimum require $g_6 > 0$.
- g_4 is now ***negative***. $g_4 = -|g_4|$
- $g_2 = \gamma(T - T_o)$, where $\gamma > 0$ and T_o is a constant (NB: T_o is smaller than the Curie temperature for first order transitions)

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Spontaneous polarisation in first order transitions

Minimising G_{FE} w.r.t P:

$$\frac{\partial G_{FE}}{\partial P} = P\underbrace{(g_2 + g_4 P^2 + g_6 P^4)}_{\text{quadratic in } P^2}=0$$

Two possible solutions for spontaneous polarisation:

(i) $P_s = 0$ (paraelectric state)

(ii) $P_s^2 = \frac{-g_4 \pm \sqrt{g_4^2 - 4 g_6 g_2}}{2 g_6}$ (ferroelectric state; select solution with a free energy minimum)

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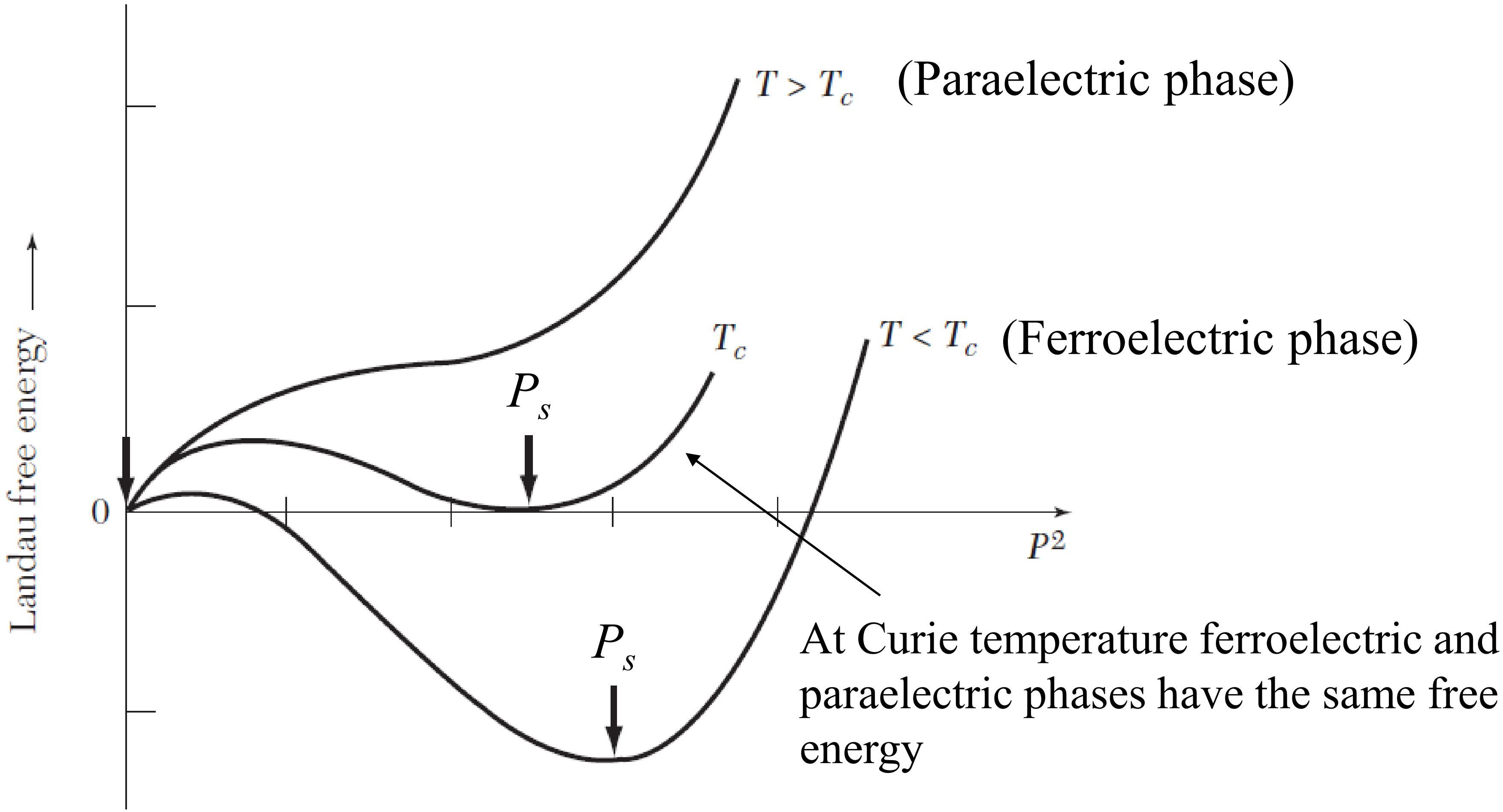
Ginzburg-Landau theory (*first* order transitions)

Plot free energy as a function of polarisation:



Note discontinuous change in spontaneous polarisation at T_c (cf. second order transitions)

End of Part 2!

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