Landau Theory for Ferroelectrics

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2017-12-01

Xu Group Meeting

Landau Models

- Landau-Devonshire: infinite (no boundaries) & uniform polarization
- Landau-Ginzburg: infinite & non-uniform polarization
- Landau Ginzburg w/ BCs: most realistic to thin films

Phenomenology	**Ferroelectric (near T_c)**
Landau - Devonshire Theory (Uniform Polarization)	Poled Bulk System
Landau-Ginzburg Theory (Polarization with Spatial Gradient)	Bulk System
Landau-Ginzburg Theory with Boundary Conditions	Film

Built-in Fields in FTJs

- See in our STO/LSMO/BTO systems
  - Asymmetric hysteresis loops
- Theoretical work using free-energy
  - What are all these terms?

PHYSICAL REVIEW B **88**, 024106 (2013)

Effect of a built-in electric field in asymmetric ferroelectric tunnel junctions

Yang Liu,[1,2,*] Xiaojie Lou,[1] Manuel Bibes,[3] and Brahim Dkhil[2]

$$F = h\Phi + \Phi_S = \left(\frac{1}{2}\alpha_1^* P^2 + \frac{1}{4}\alpha_{11}^* P^4 + \frac{1}{6}\alpha_{111} P^6 + \frac{1}{8}\alpha_{1111} P^8 + \frac{u_m^2}{S_{11}+S_{12}} - \frac{1}{2}\vec{E}_{\text{dep}} \cdot \vec{P} - \vec{E}_{bi} \cdot \vec{P} - \vec{E} \cdot \vec{P}\right) h + (\zeta_1 - \zeta_2)\vec{n} \cdot \vec{P} + \frac{1}{2}(\eta_1 + \eta_2) P^2,$$

Built-in Fields in FTJs

- (i) Bulk free energy
- (ii) Depolarization energy
- (iii) Build-in field due to electrodes
- (iv) Surface energy

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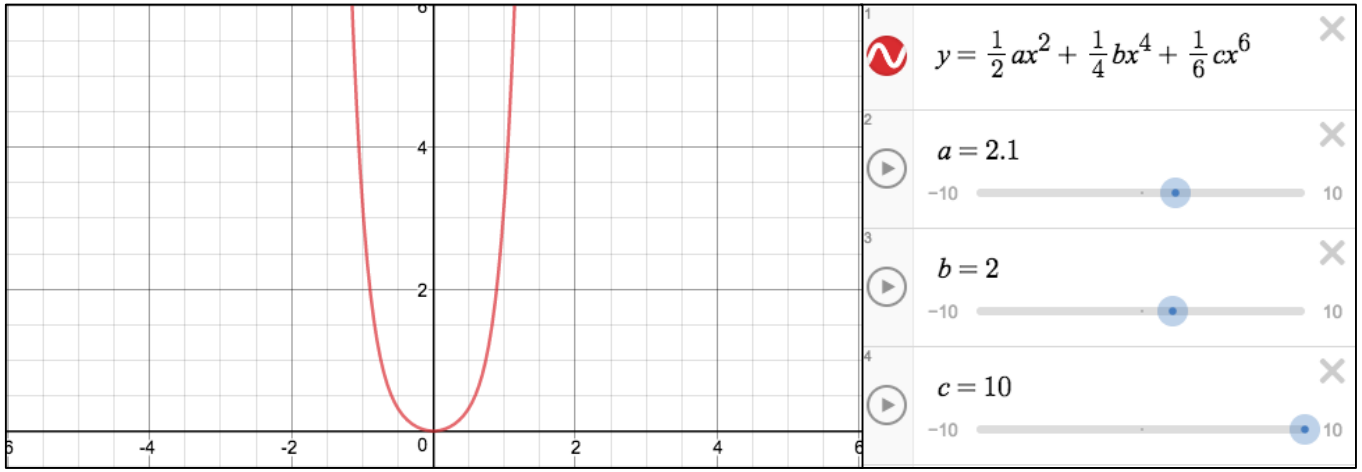
Landau-Devonshire Treatment

- $\mathcal{F}_p = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 - EP$
  - Equilibrium: $E = aP + bP^3 + cP^5$
  - $a = a_0(T - T_0)$ based on Curie susceptibility

- Paraelectric: a>>0



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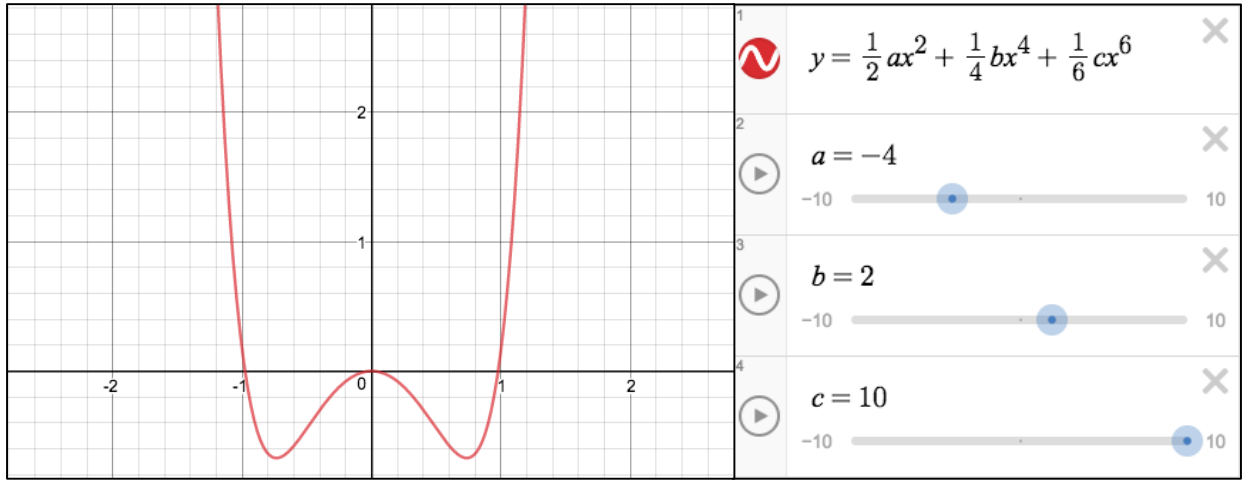

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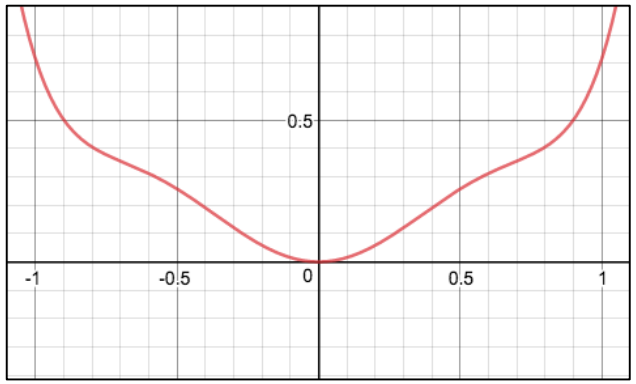
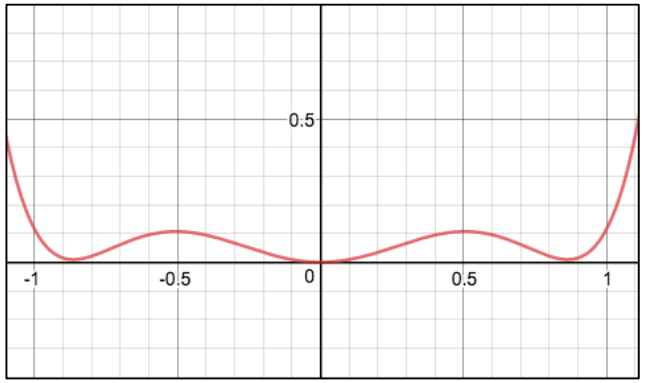
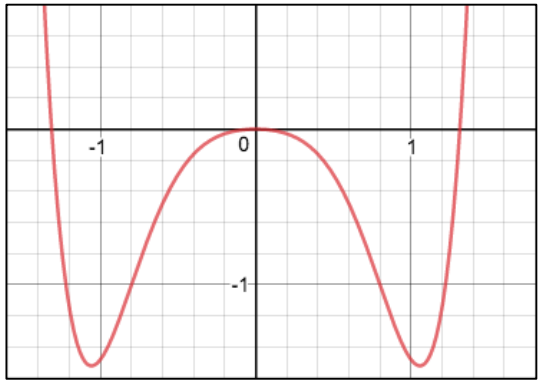
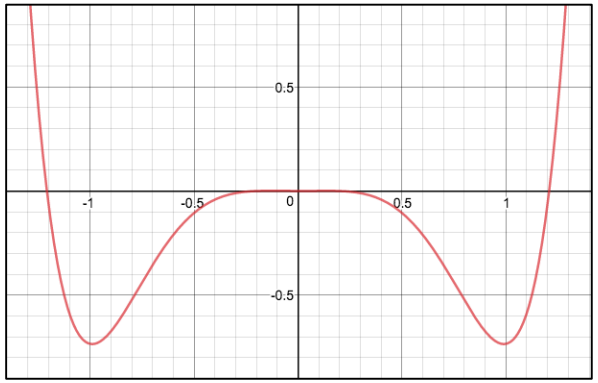
- Paraelectric: a>>0
- Ferroelectric: a<<0
- b affects type of transition









Coupling to Strain

- $\mathcal{F} = \mathcal{F}_P + \mathcal{F}_\eta$
  - $\mathcal{F}_\eta = \frac{1}{2}K\eta^2 + Q\eta P^2 + \cdots - \eta\sigma$

- Matching to lattice: η=0 so $\mathcal{F}_\eta = 0$
- No external stress: σ=0 so $\eta = -\frac{QP^2}{K}$
  - $\mathcal{F} = \frac{1}{2}aP^2 + \frac{1}{4}\left(b - \frac{2Q^2}{K}\right)P^4 + \frac{1}{6}cP^6 - EP$
  - Strain-coupling can lead to change in *type* of phase transition

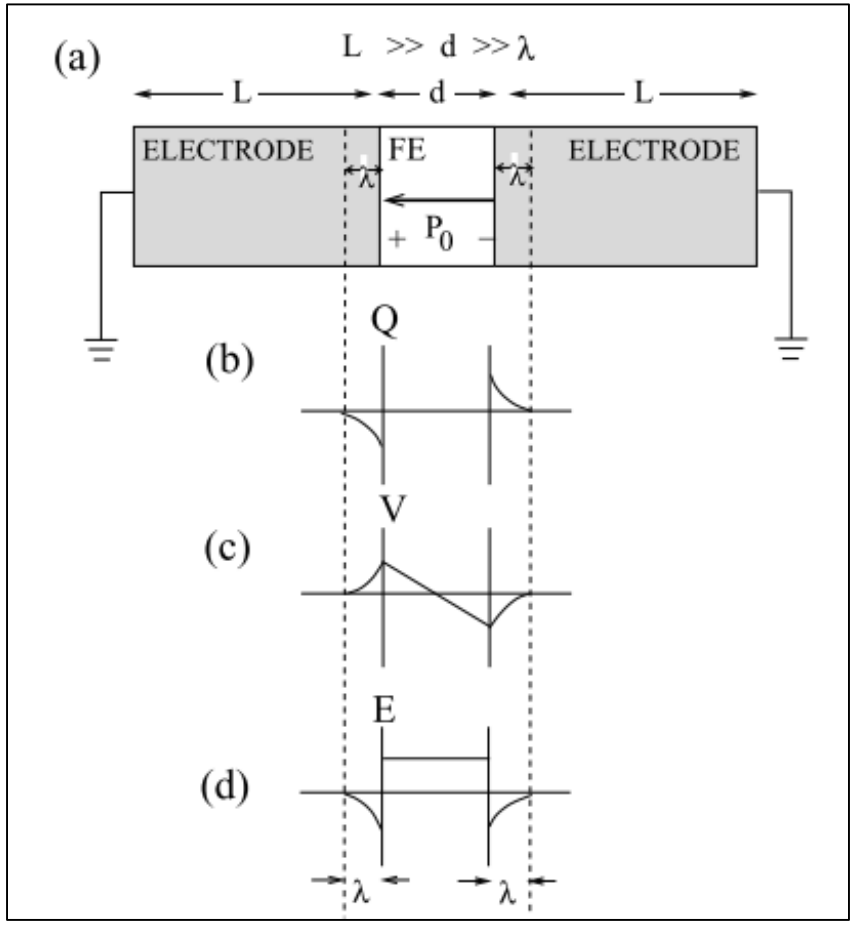
Landau-Ginzburg Treatment

- Landau-Devonshire + small polarization fluctuations
  - Non-uniform P in bulk
- Integrate polarization over volume for free energy determination
- Correlation functions:
  - $g(r) = \frac{k_B T}{\gamma} \frac{e^{-\frac{r}{\xi}}}{r^{d-2}}$ $(T \neq T_0)$
  - $g(r) = \frac{k_B T}{\gamma} \frac{1}{r^{d-2}}$ $(\mathrm{T} = T_0)$

Depolarization Effects

- Finite charge screening length λ
  - Voltage drop across electrodes leads to field in FE layer

- $E_{dep} = E_0 - \frac{P}{\epsilon_0} = \frac{P}{\epsilon_0}\left(\frac{1}{1+\frac{2\lambda}{d}} - 1\right)$
  - $\sim \frac{2P\lambda}{\epsilon_0 d}$ for P uniform and λ<<d



Treatment of Strained Films

$$\mathcal{F} = \mathcal{F}_P - \frac{1}{2}s_{11}(\sigma_1^2 + \sigma_2^2) - Q_{12}\{(\sigma_1 + \sigma_2)P^2\} - s_{12}\sigma_1\sigma_2 - \frac{1}{2}s_{44}\sigma_6^2$$

- Considering a film grown on a substrate with lattice-mismatch
  - $\frac{a-a_0}{a} \neq 0$
- Cubic film on cubic substrate:
  - $\sigma_3 = \sigma_4 = \sigma_5 = 0$; no external stress on z-face of film
- s_{ij}: elastic compliance coefficients; can relate to ”stiffness” of film

Magic Happens…

- Very opaque to me
- Hooke's law-like terms
- Polarization-dependence
- Some cross-terms?
- Why?
- Who knows?

$$\tilde{\mathcal{F}} = \mathcal{F} + \eta_1\sigma_1 + \eta_2\sigma_2 + \eta_6\sigma_6 \tag{76}$$

must be performed in order to study the equilibrium properties of this constrained film.

For pedagogical simplicity, we consider a uniaxial ferroelectric where P is the polarization in the z-direction. The free energy, with condition (77), of a cubic ferroelectric is [98]

$$\mathcal{F} = \mathcal{F}_P - \boxed{\frac{1}{2}s_{11}(\sigma_1^2 + \sigma_2^2)} - \boxed{Q_{12}\{(\sigma_1 + \sigma_2)P^2\}} - \boxed{s_{12}\sigma_1\sigma_2 - \frac{1}{2}s_{44}\sigma_6^2} \tag{77}$$

where Q_{ij} and s_{ij} are the electrostrictive constants and the elastic compliances at constant polarization respectively. Using $\frac{\partial \mathcal{F}}{\partial \sigma_i} = -\eta_i$, and solving for $\sigma_1 = \sigma_2 = \bar{\sigma}$ (in this special case $\sigma_6 = 0$), we find that

$$\boxed{\tilde{\mathcal{F}} = \frac{\bar{\eta}^2}{s_{11} + s_{12}} + \frac{1}{2}\tilde{a}P^2 + \frac{1}{4}\tilde{b}P^4 + \frac{1}{6}cP^6} \tag{78}$$

where

$$\tilde{a} = a - \frac{4\bar{\eta}Q_{12}}{s_{11} + s_{12}} \tag{79}$$

and

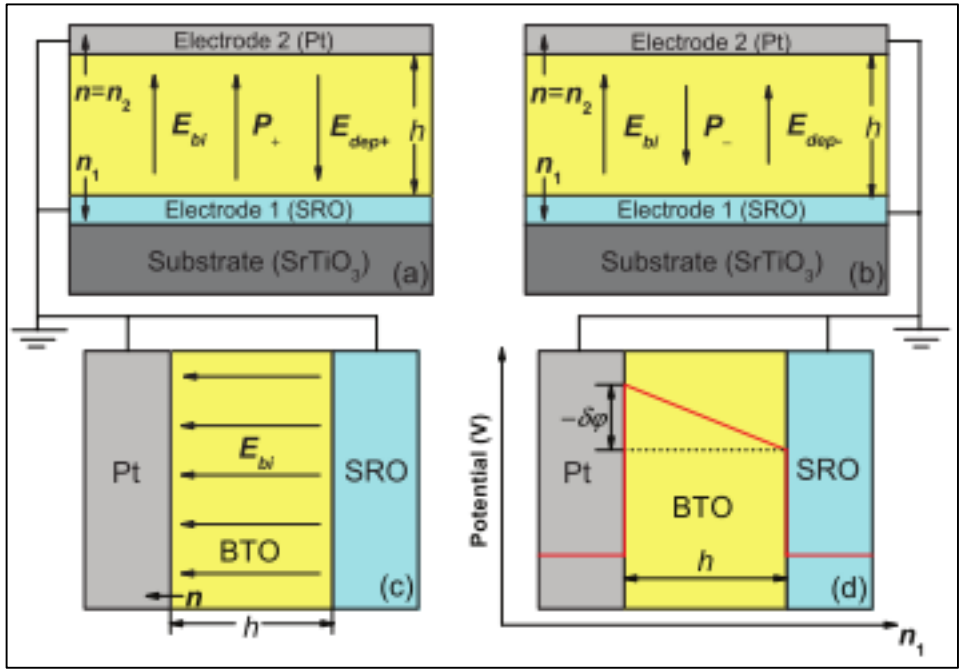
$$\tilde{b} = b + \frac{4Q_{12}^2}{s_{11} + s_{12}} \tag{80}$$

Surface Energy Terms

- Surface terminations break symmetry and thus introduce additional energies
- Perform expansion in orders of P
  - Linear term $\propto \vec{P} \cdot \hat{n}$ at both surfaces
  - Quadratic $\propto P^2$ at both surfaces

Built-in Field

- Potential difference (work function) exists at interface between FE and electrodes
- $E_{bi} = -\frac{\Delta\varphi}{h}\hat{n}$
- Only exists in asymmetric FTJs
  - Symmetric: $\varphi_1 = \varphi_2; \Delta\varphi = 0$



Thank you