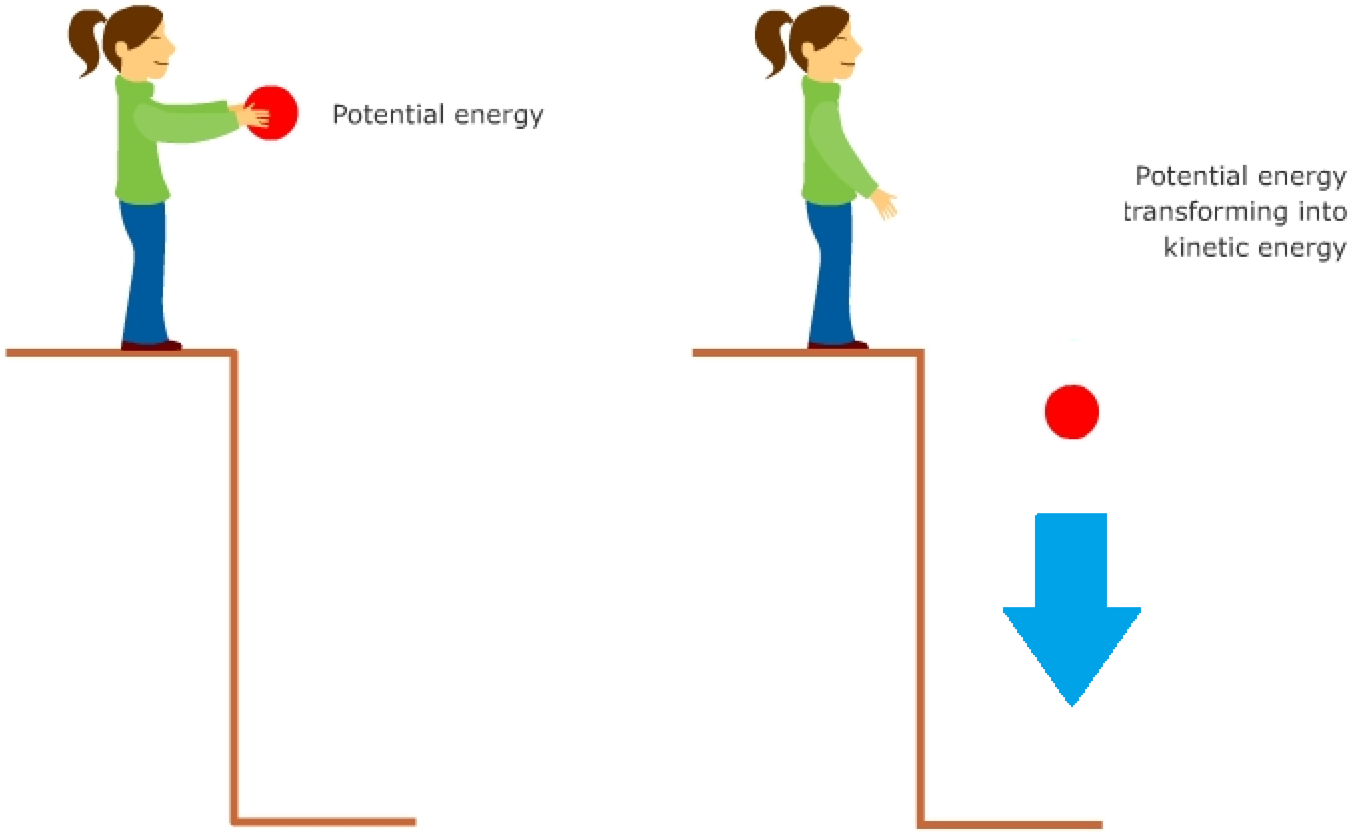
Thermodynamics of Ferroelectrics

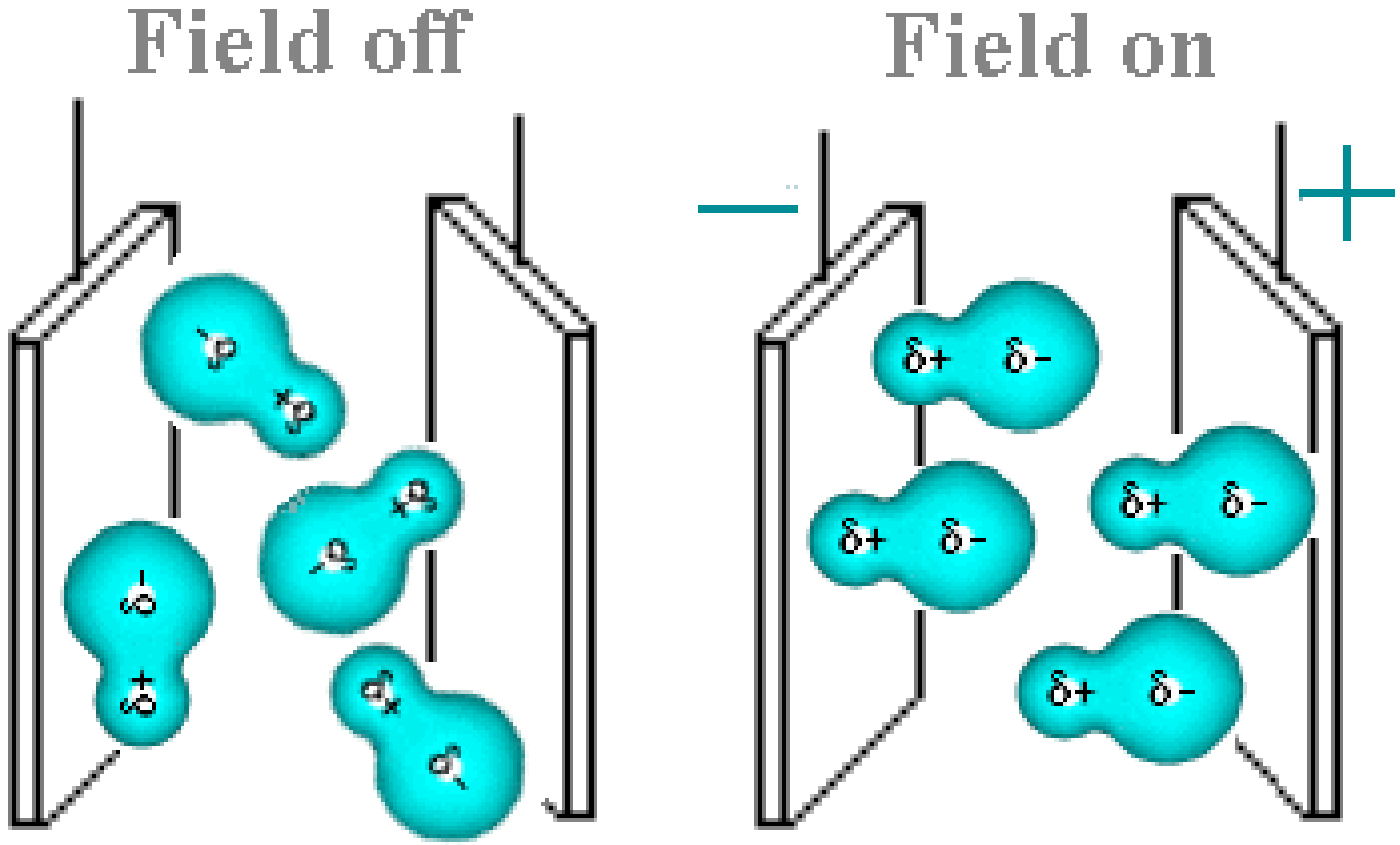
Geoffrey Xiao

Universe tends towards lower energy



https://www.pathwayz.org/Tree/Plain/ENERGY+CONSERVATION+%5BCALCULATIONS%5D

Universe tends towards lower energy

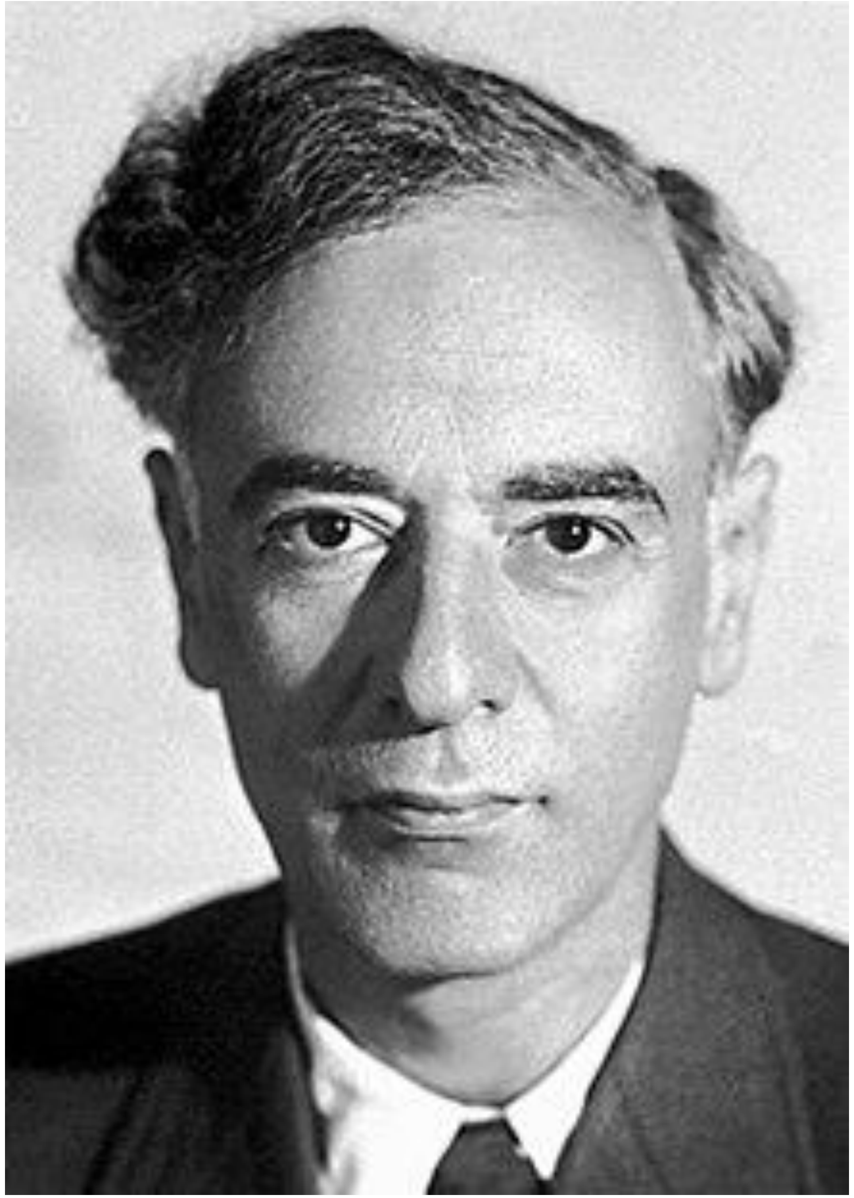


http://nobel.scas.bcit.ca/wiki/index.php/Bond_dipole_moment

Landau Free Energy

- $F = a_0 + a_1\Psi^2 + a_2\Psi^4 + \cdots$
- Ψ = Order Parameter
  - Characterize the transition
  - Ψ = 0 above the transition temperature
  - Polynomial order depends on symmetry

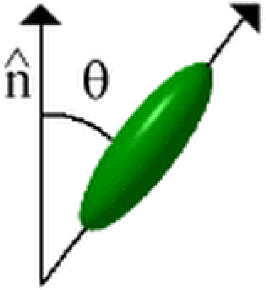
1962 Nobel Prize in Physics

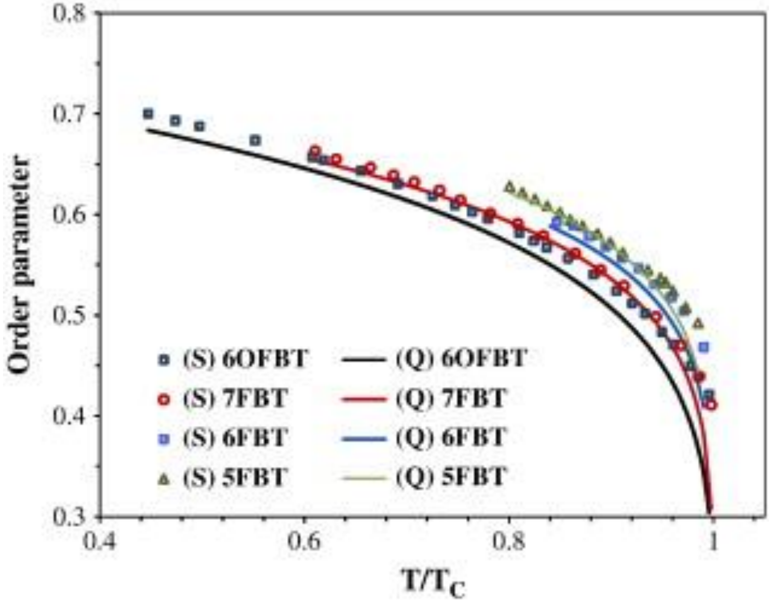


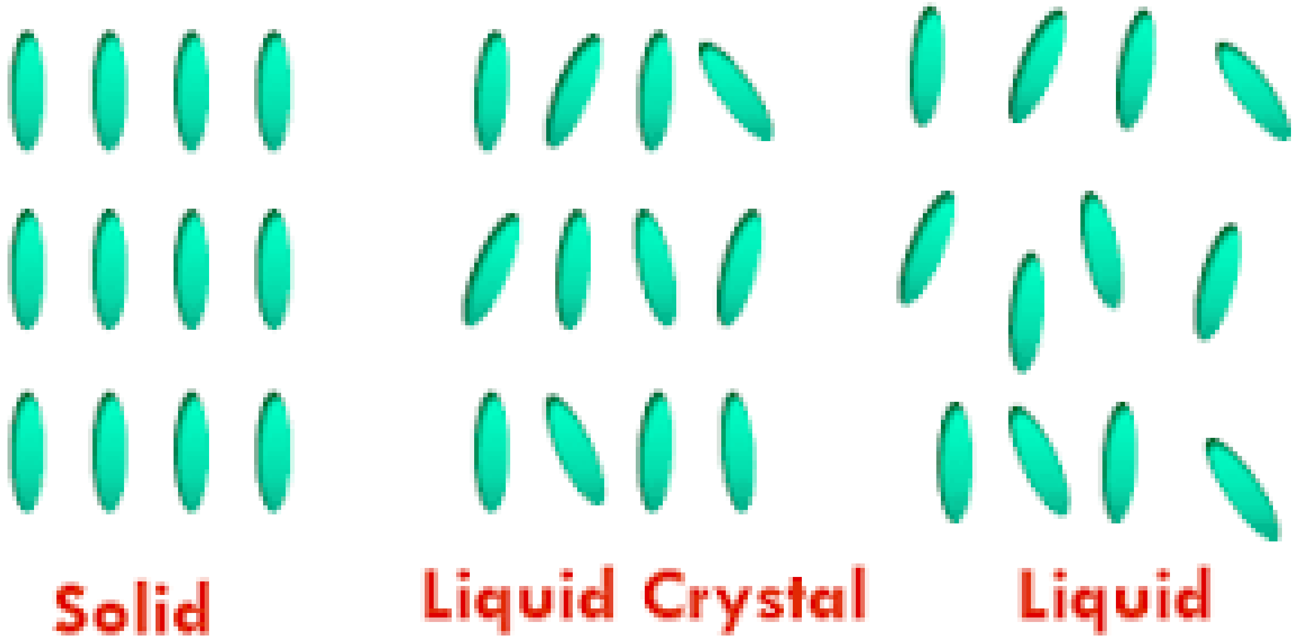
https://en.wikipedia.org/wiki/Lev_Landau

Liquid Crystals

- $\Psi = < \frac{3\cos^2\theta - 1}{2} >$







$\Psi \neq 0$

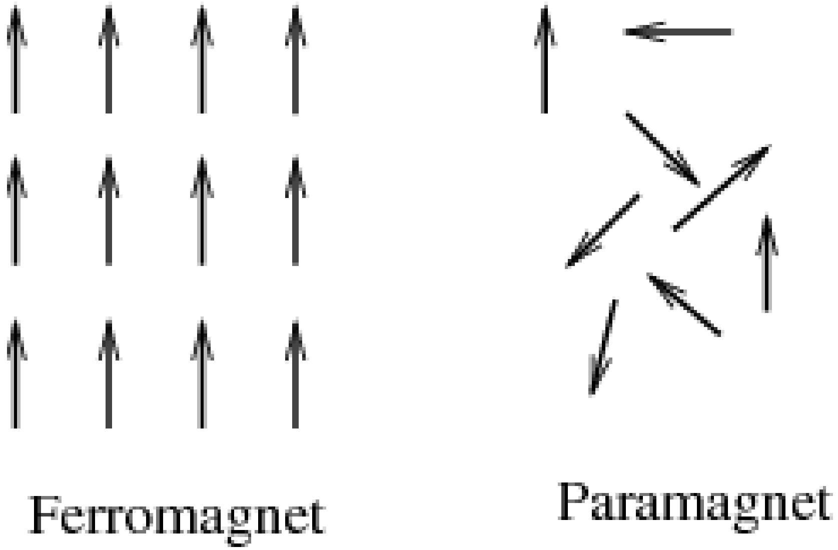
$\Psi = 0$

https://chemistry.tutorvista.com/analytical-chemistry/liquid-polymer.html
http://pharmalife.weebly.com/blog/liquid-crystal-state
Journal of Molecular Liquids, Volume 157, Issues 2–3, 30 November 2010, Pages 119-124

https://ps.uci.edu/~cyu/p115A/LectureNotes/Lecture19/html_version/lecture19.html
The Review of scientific instruments 83(6):066106, June 2012

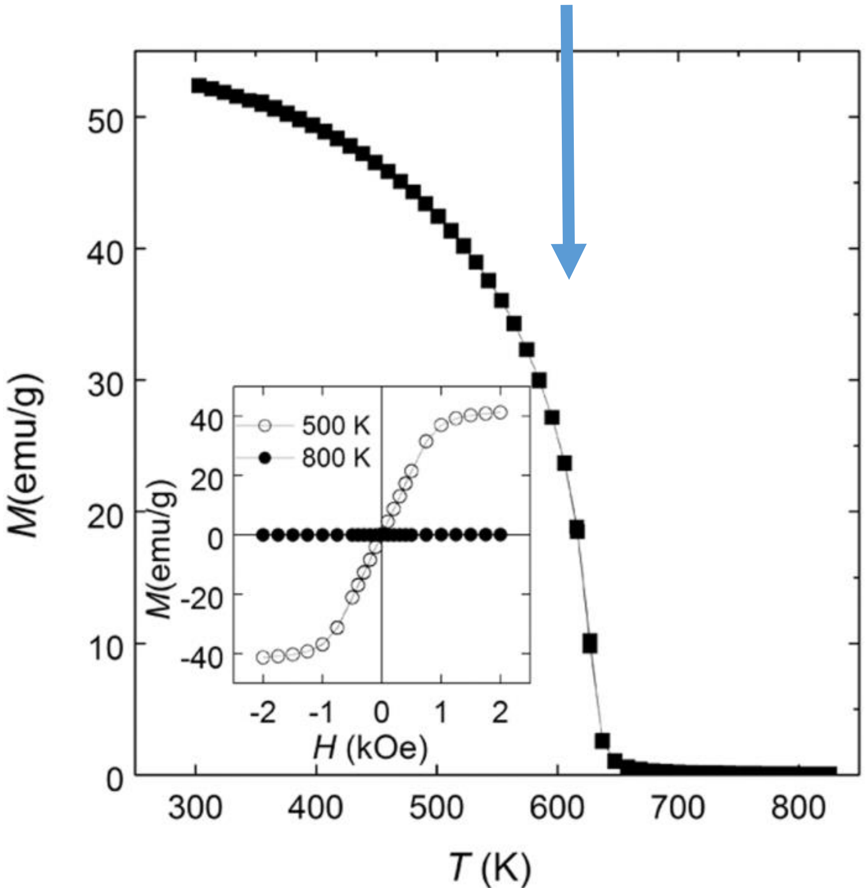
Ferromagnet

- Permanent magnet
- $\Psi = \|\vec{M}\|$
- $\vec{M}$ = magnetization vector



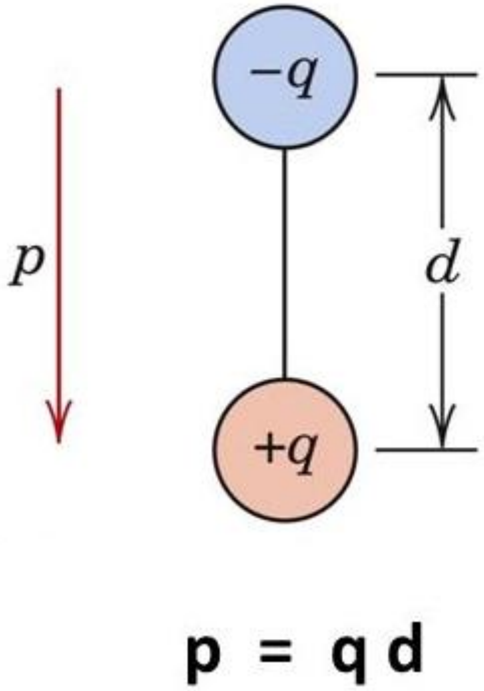
$\Psi \neq 0$ $\qquad$ $\Psi = 0$

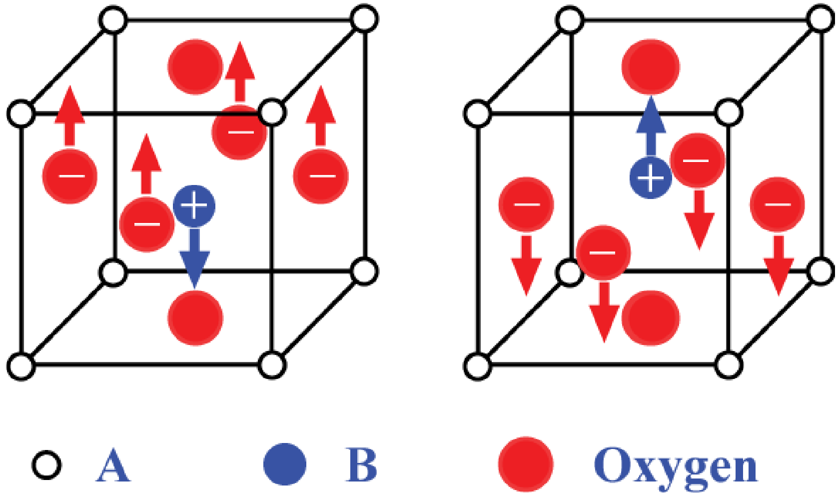
Curie Temperature



Ferroelectric

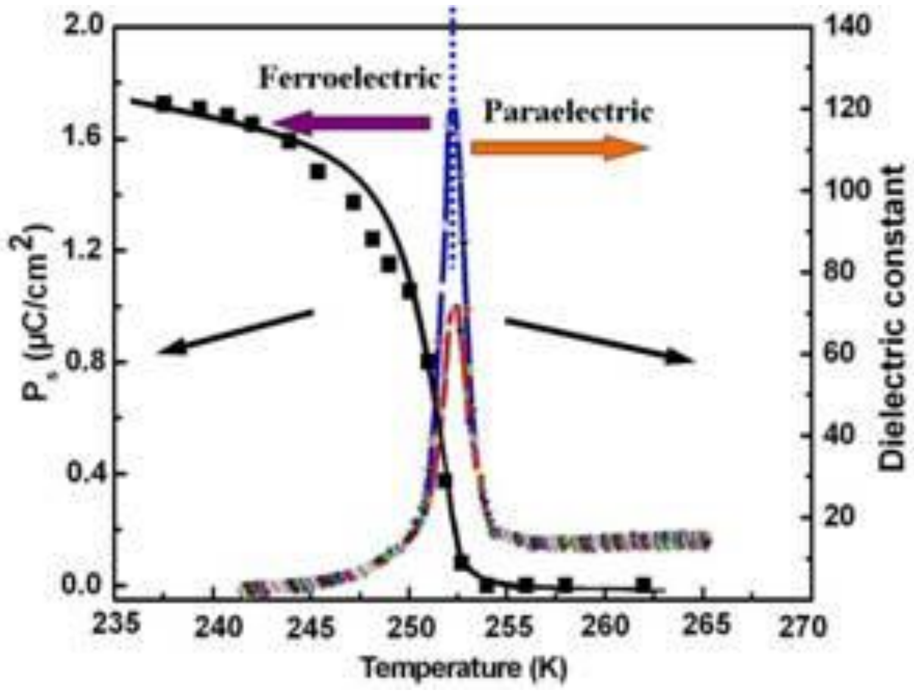
- Permanent electric dipole
- $\Psi = \|\vec{P}\|$
- $\vec{P}$ = Polarization vector

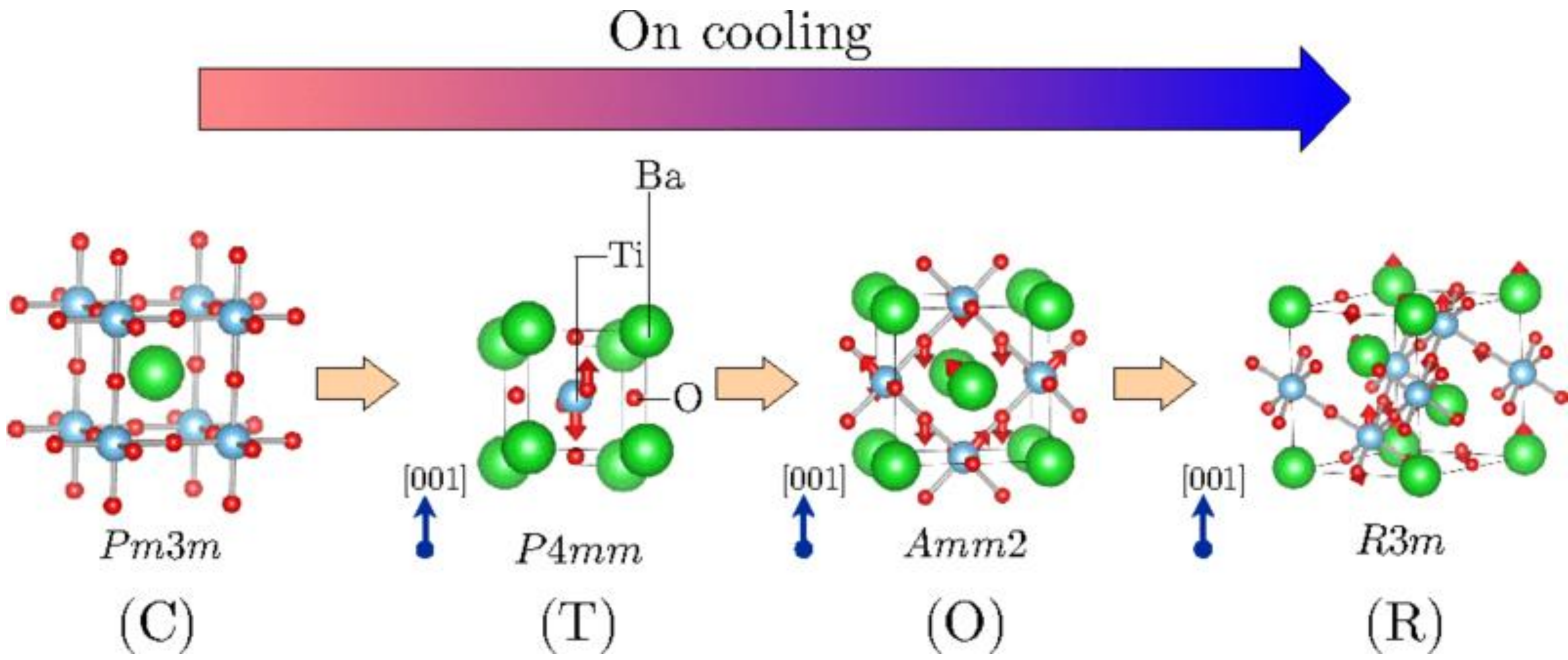




http://slideplayer.com/slide/6653427/
http://www.eedevice.com/research.html

Ferroelectric





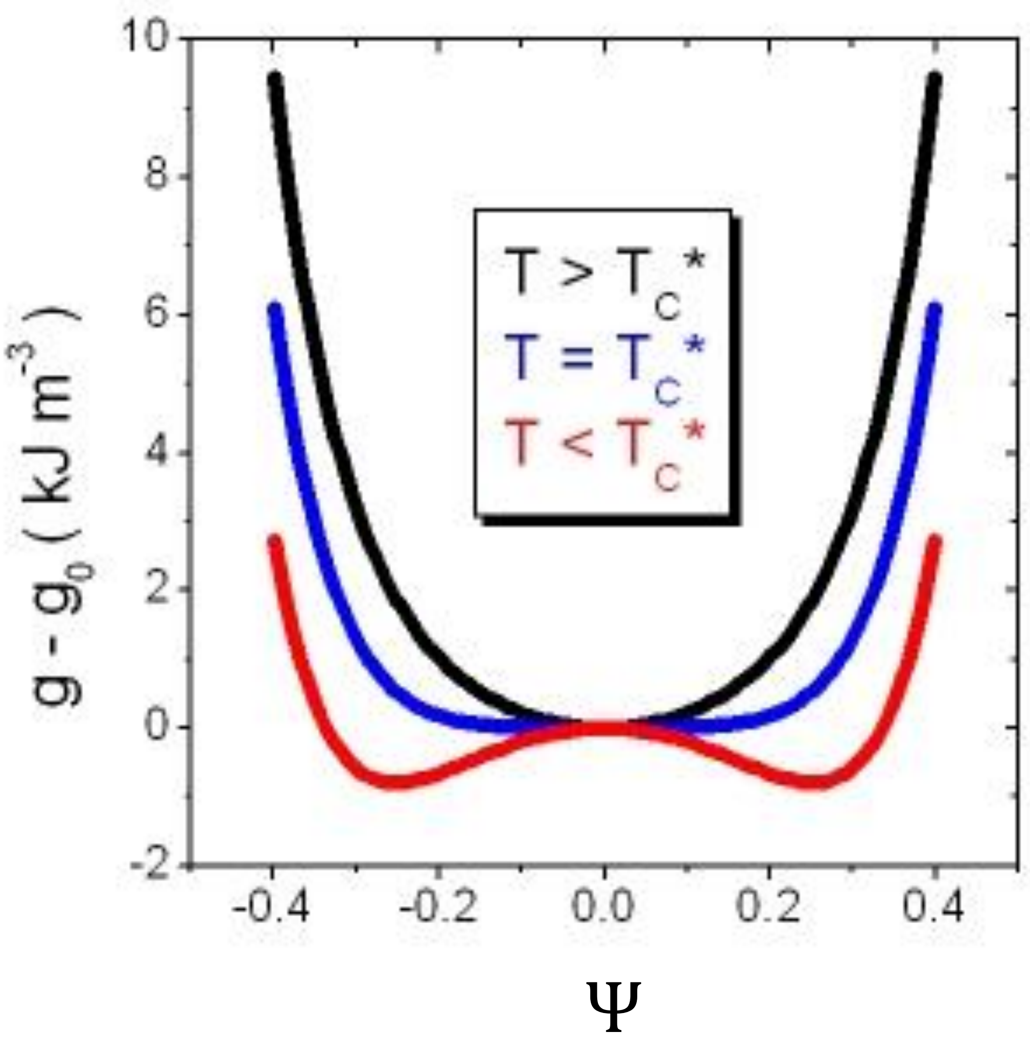
$\Psi = 0$

$\Psi \neq 0$

Phys. Rev. B **93**, 144111 – Published 11 April 2016
http://english.fjirsm.cas.cn/rh/rps/201202/t20120213_81292.html

Landau Free Energy

- $F = a_0 + a_1\Psi^2 + a_2\Psi^4 + \cdots$
- Energy minimization!
  - Above $T_C \rightarrow \Psi = 0$
  - Below $T_C \rightarrow$ Symmetry breaking

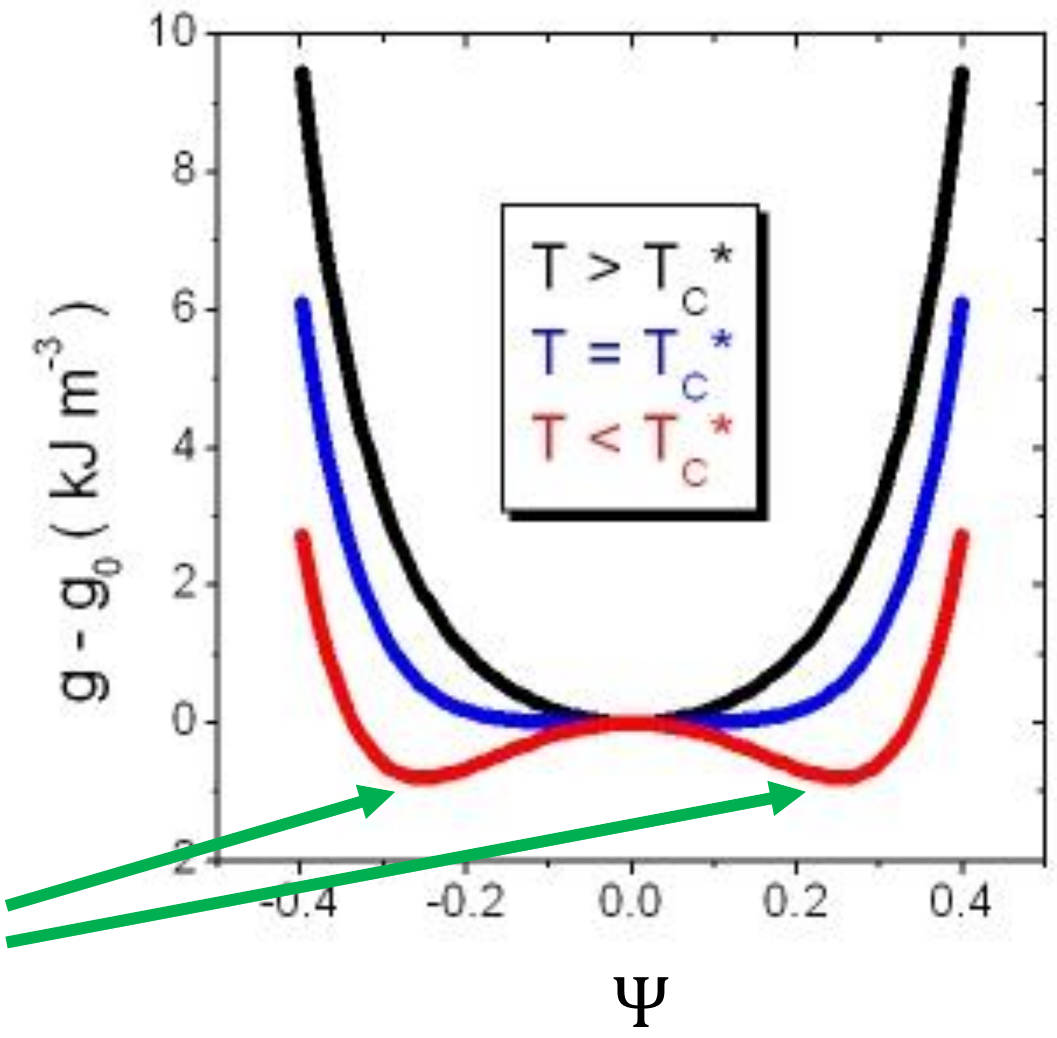


http://www.ndlc.physics.manchester.ac.uk/people/staff/archer/Landau%20potential/

Symmetry

- Degeneracy of stable states when $T < T_C$

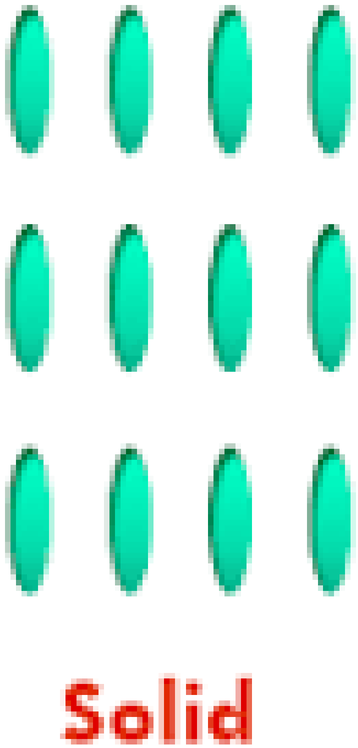
Symmetry breaking



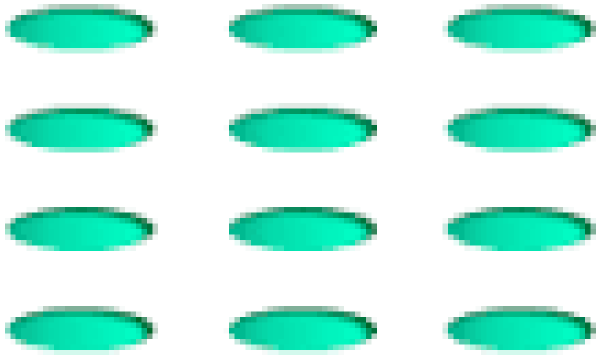
http://www.ndlc.physics.manchester.ac.uk/people/staff/archer/Landau%20potential/

Liquid Crystals

- Absent an external field



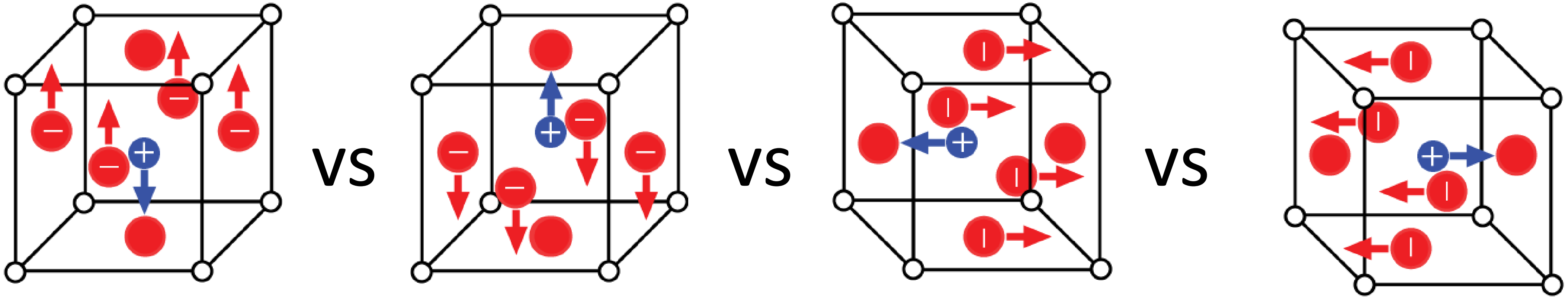
vs



https://chemistry.tutorvista.com/analytical-chemistry/liquid-polymer.html

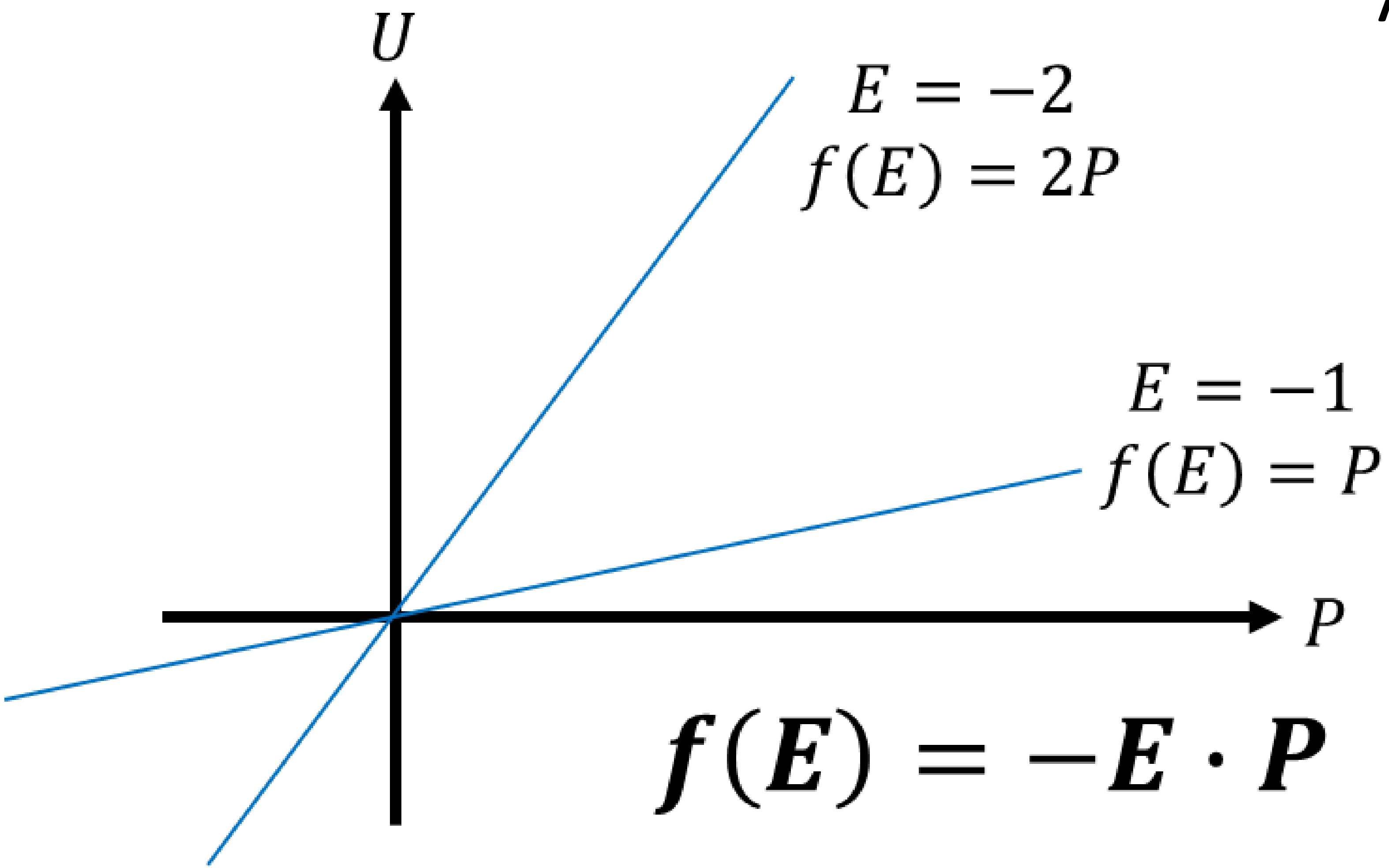
Ferroelectric

- Symmetry breaking = system adopts one of the symmetric states
- $F = a_0 + a_1\Psi^2 + a_2\Psi^4 + \cdots$
- Symmetry → Why free energy expansion only has even polynomials

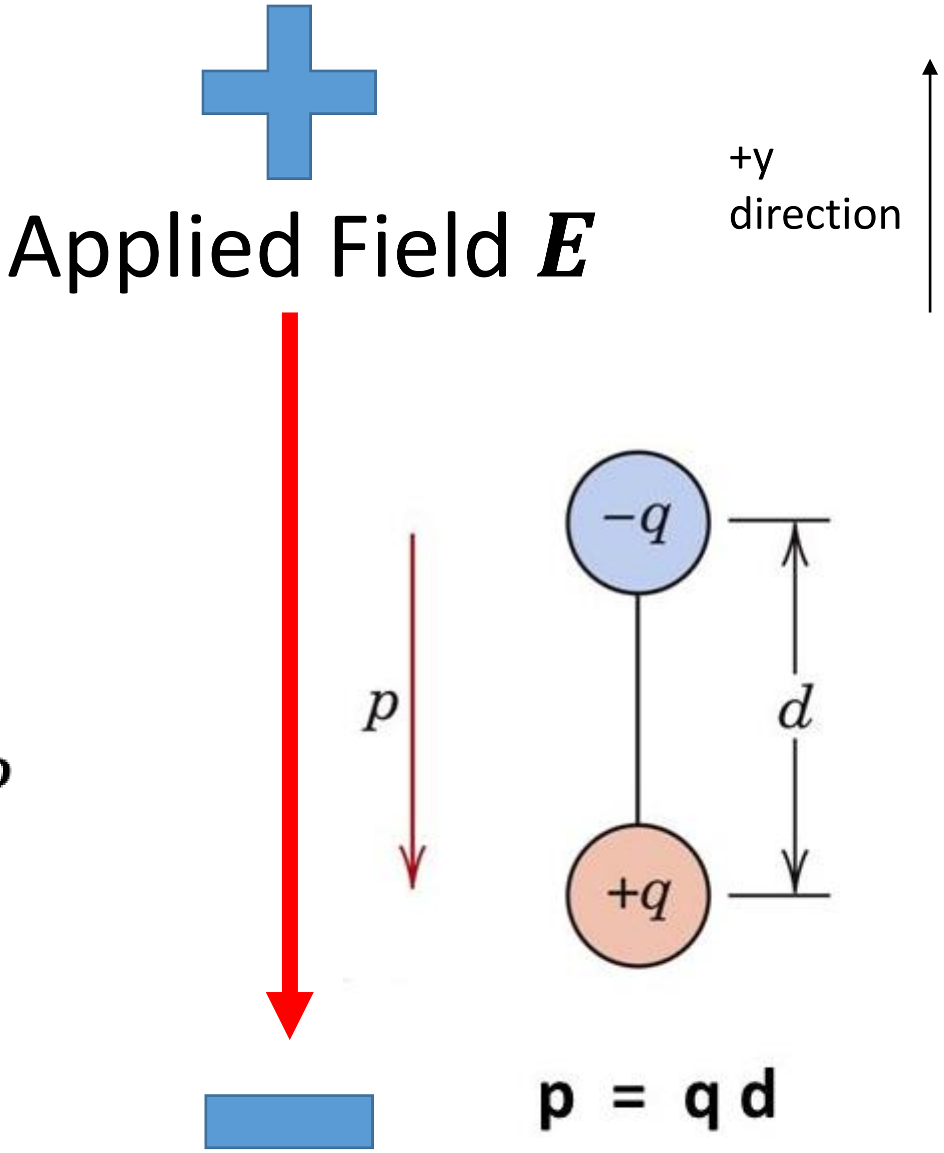


http://slideplayer.com/slide/6653427/
http://www.eedevice.com/research.html

Electrical Energy



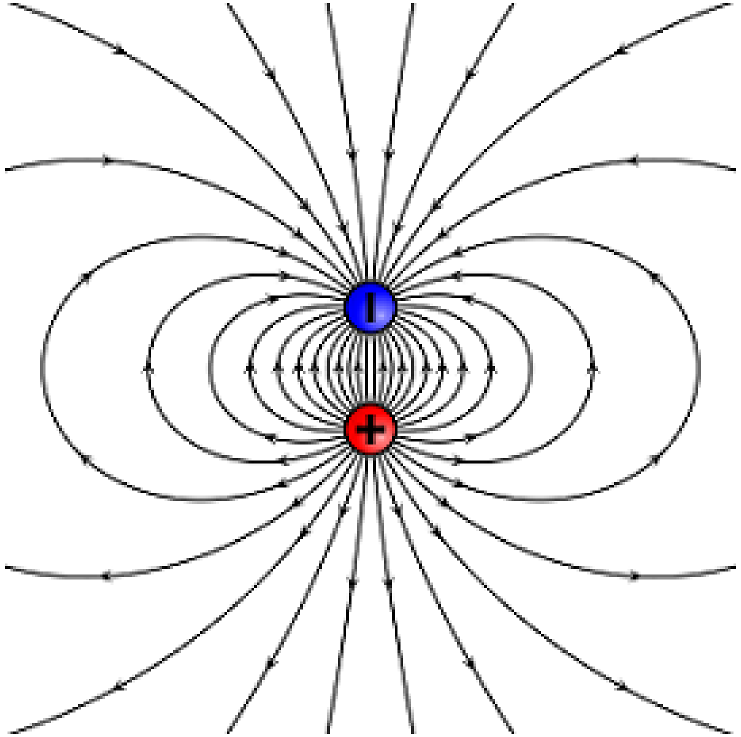
$$\boldsymbol{f(E) = -E \cdot P}$$

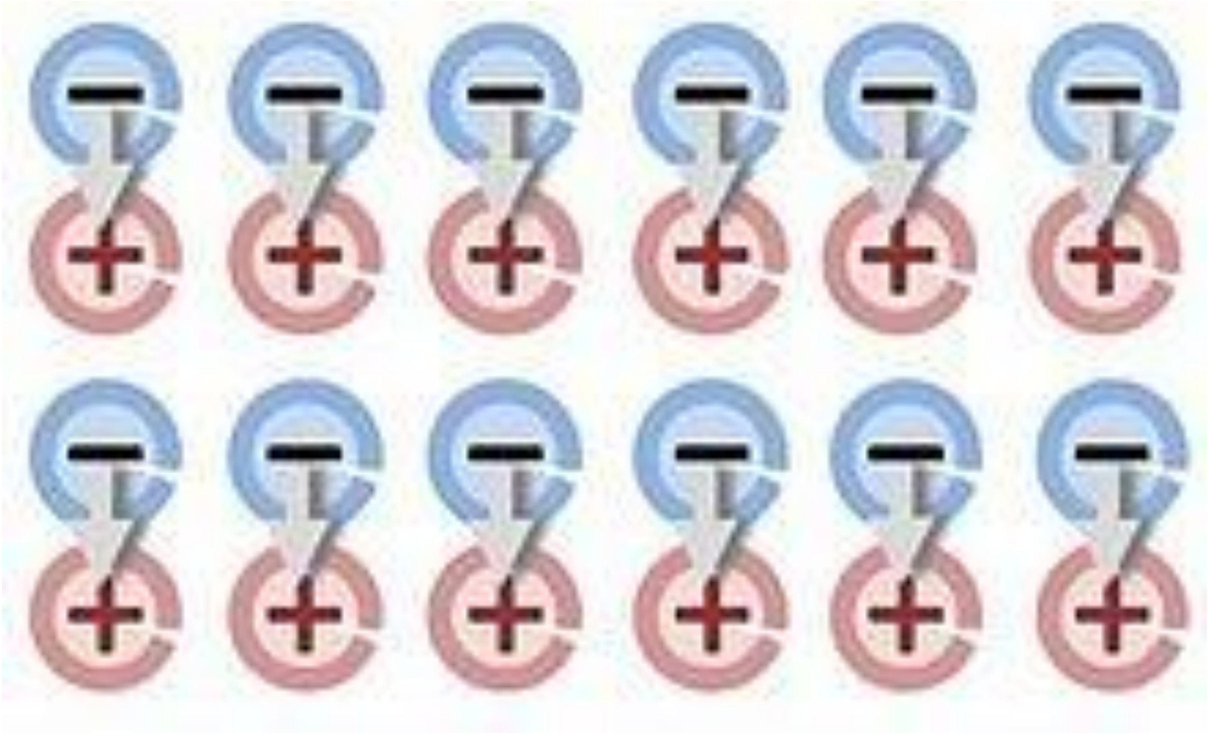


http://slideplayer.com/slide/6653427/

Long Range Electrical Energy

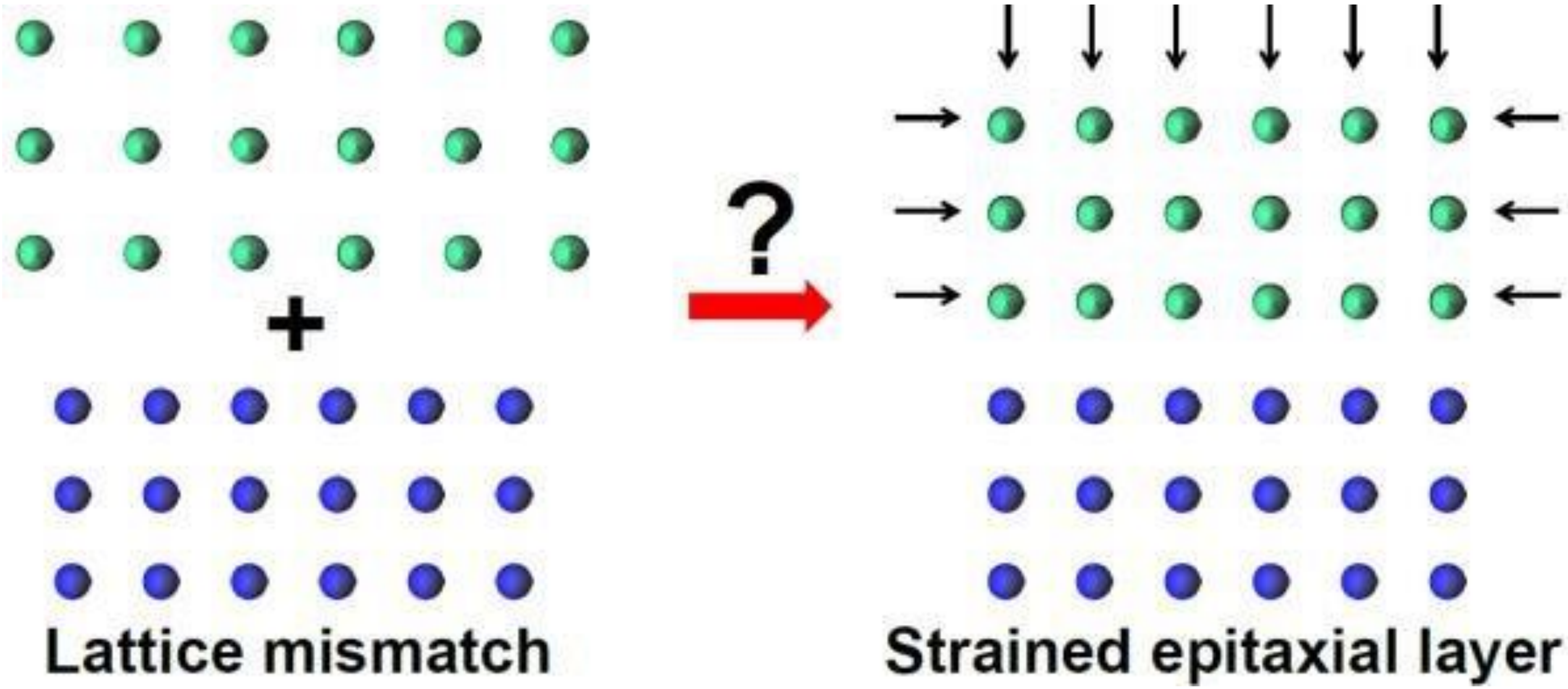
- Each dipole produces a field
- What is the total electrical energy?





https://en.wikipedia.org/wiki/Electric_dipole_moment
http://energyeducation.ca/encyclopedia/Electric_dipole

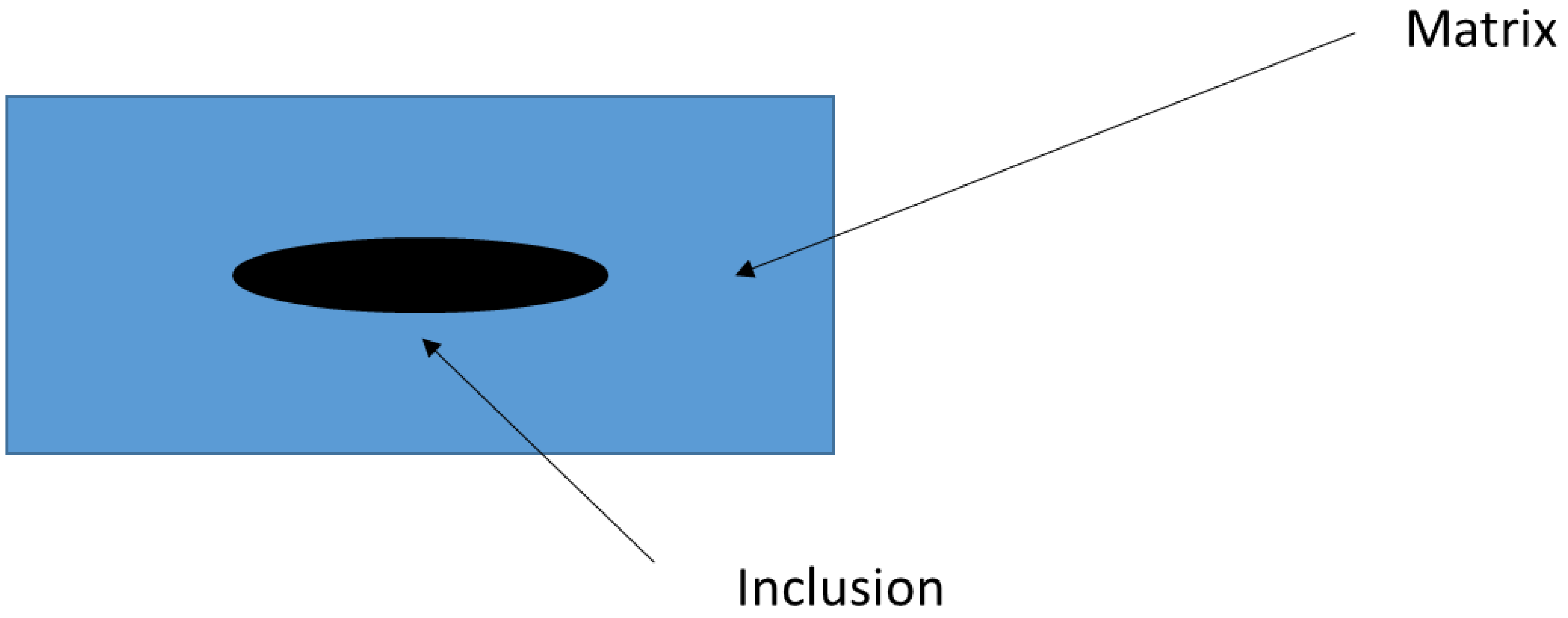
Elastic Energy



http://www.alexshluger.com/people/sanliang.htm

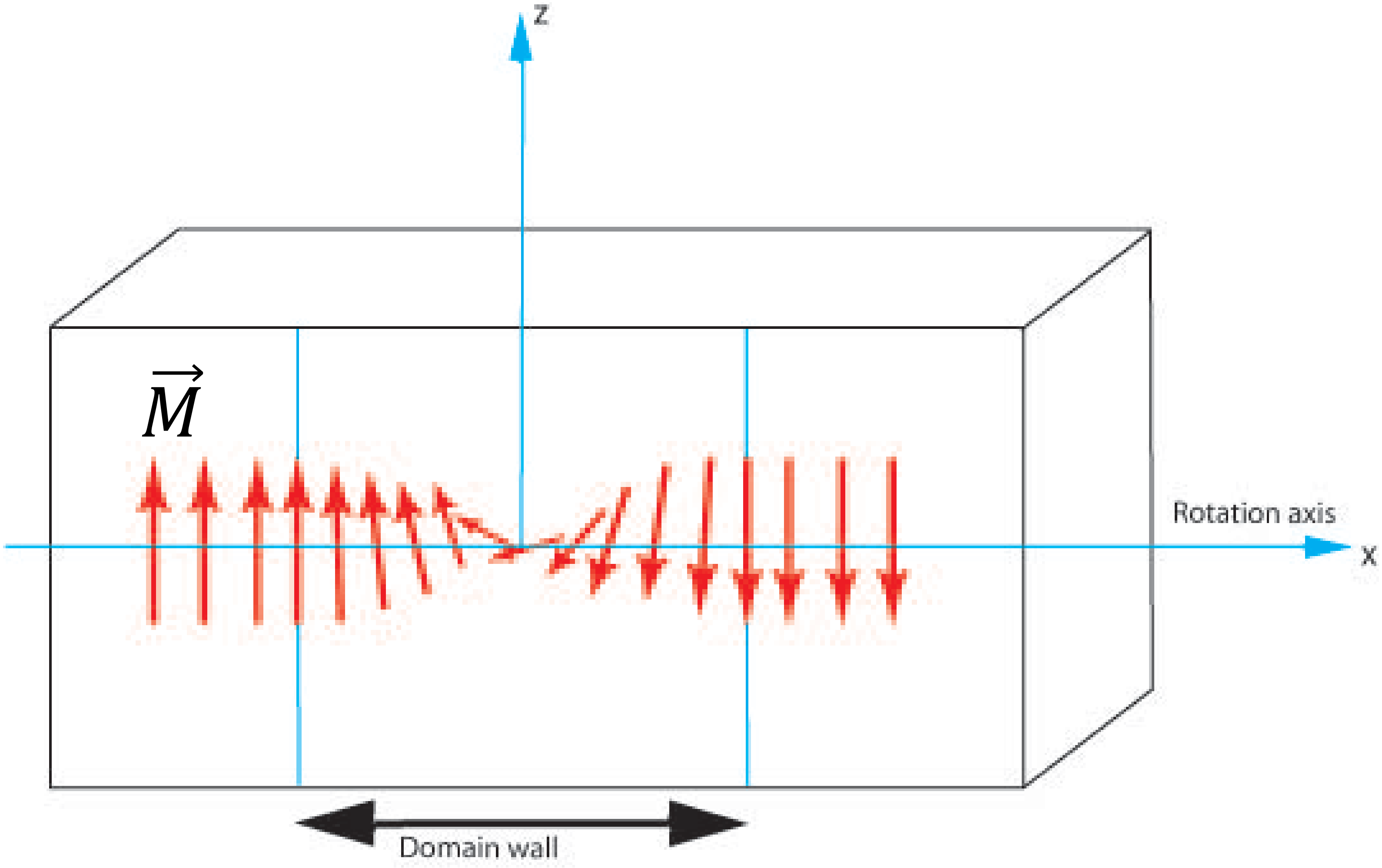
Elastic Energy

- Inclusion changes shape? What is the lattice mismatch and the elastic energy?



Interfacial Energy

- Homogeneity preferred



https://www.doitpoms.ac.uk/tlplib/ferromagnetic/walls.php

Putting it all together… Phase Field Modeling

$$F = \int f_l + f_e + f_g + f_{elec}\, dV, \frac{\partial P_i}{\partial t} = \frac{\delta F}{\delta P_i}$$

$$f_l = \frac{1}{2} a_{ij} P_i^2 P_j^2 + \frac{1}{4} a_{ijkl} P_i P_j P_k P_l + \cdots$$ Landau Energy

$$f_e = \frac{1}{2} C_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^0)(\varepsilon_{kl} - \varepsilon_{kl}^0)$$ Elastic Energy

$$f_g = \frac{1}{2} G_{ijkl} \frac{\partial P_i}{\partial x_j} \frac{\partial P_k}{\partial x_l}$$ Interfacial Energy

$$f_{elec} = -\frac{1}{2} E_i^d P_i - E_i^{app} P_i$$ Electrical Energy

<u>Equilibrium Conditions</u>

$$\sum_i \frac{\partial \sigma_{ij}}{\partial x_j} = 0$$

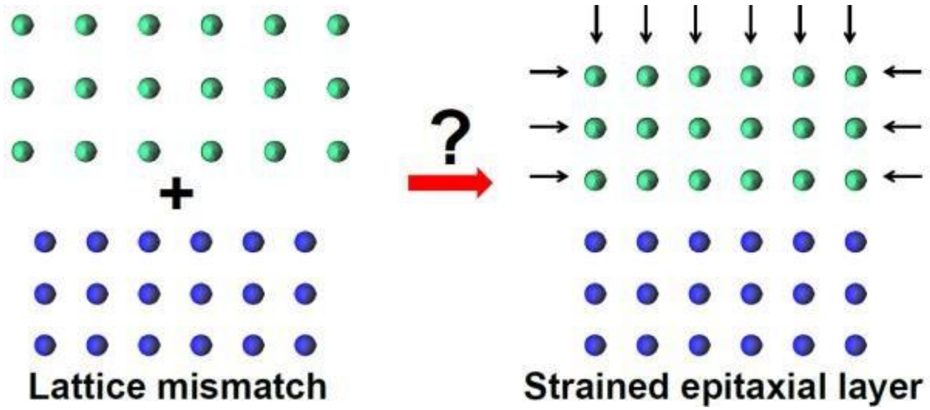
$$\sum_{i,j} \varepsilon_0 \kappa_{ij} \frac{\partial E_j^d}{\partial x_i} = \sum_i -\frac{\partial P_i}{\partial x_i}$$

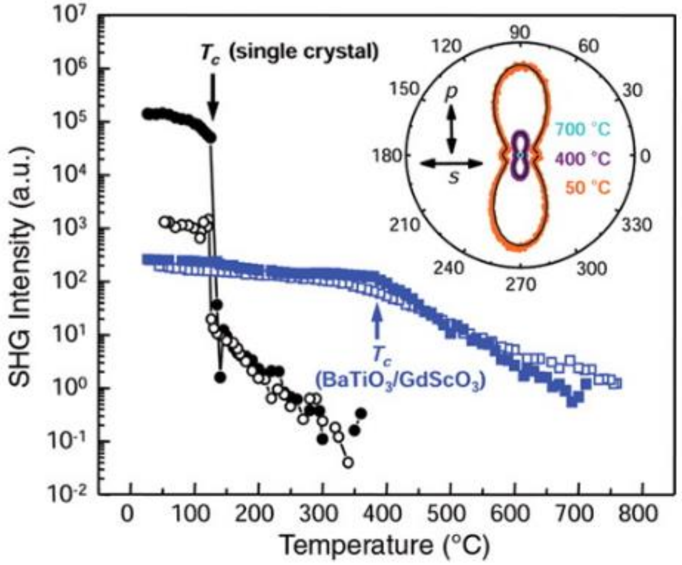
- Implemented in C and MATLAB
- 3-dimensional simulation of ferroelectric materials

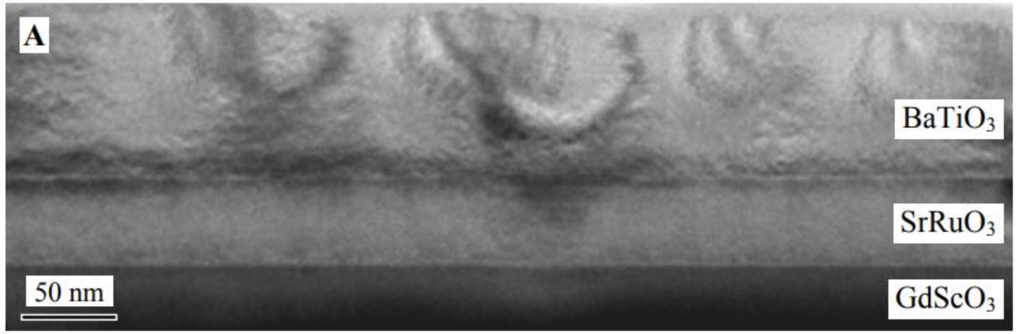
http://www.alexshluger.com/people/sanliang.htm

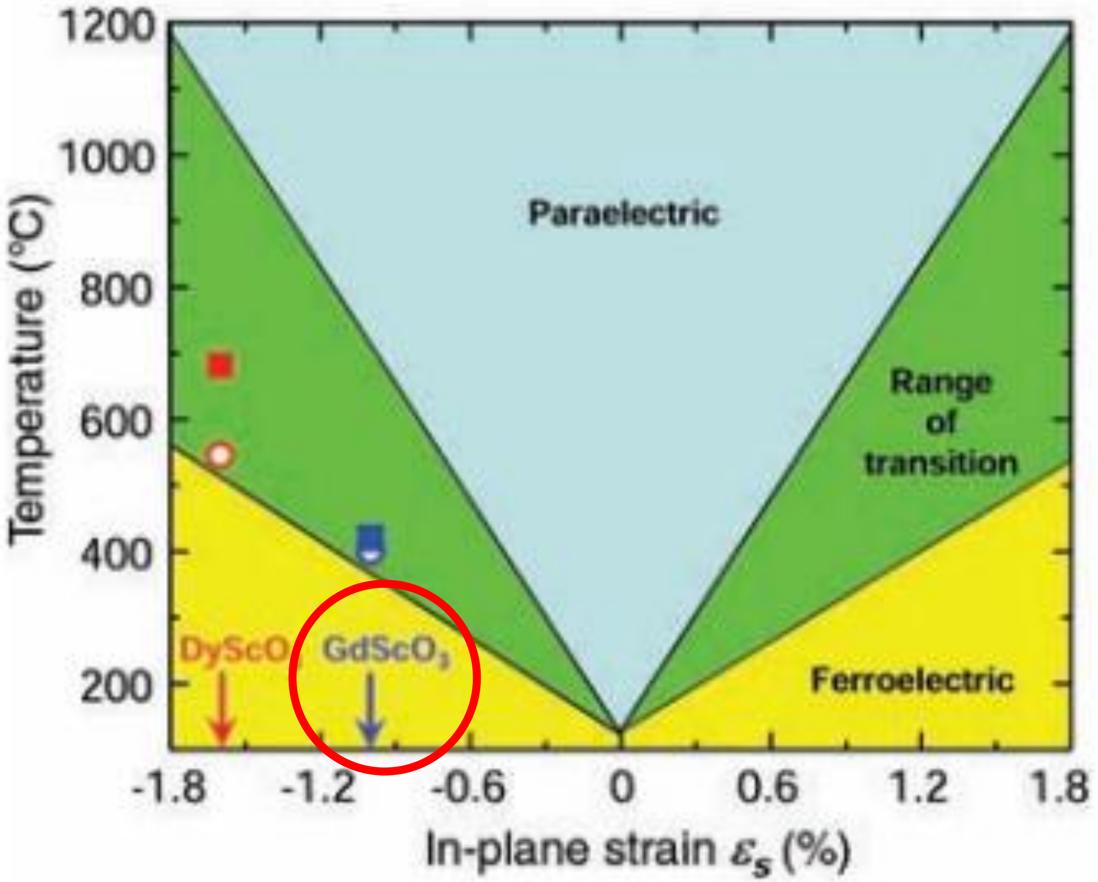
Thin Film Engineering

- Strain engineered $BaTiO_3$





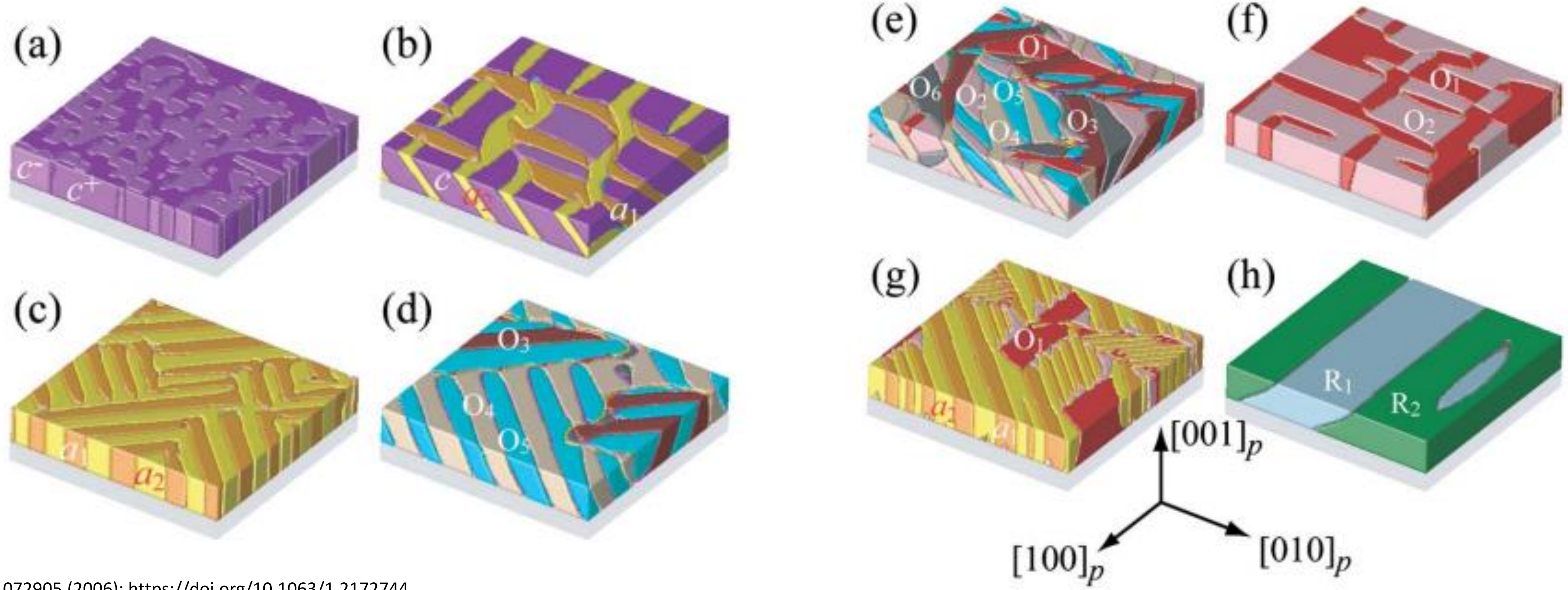




Nature volume 430, pages 758–761 (12 August 2004) doi:10.1038/nature02773

Thin Film Engineering

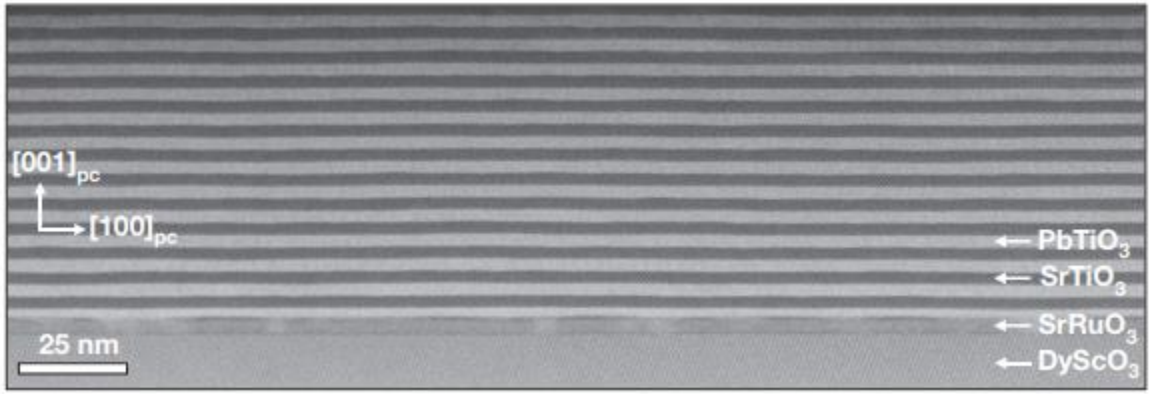
- Strain engineered thin films

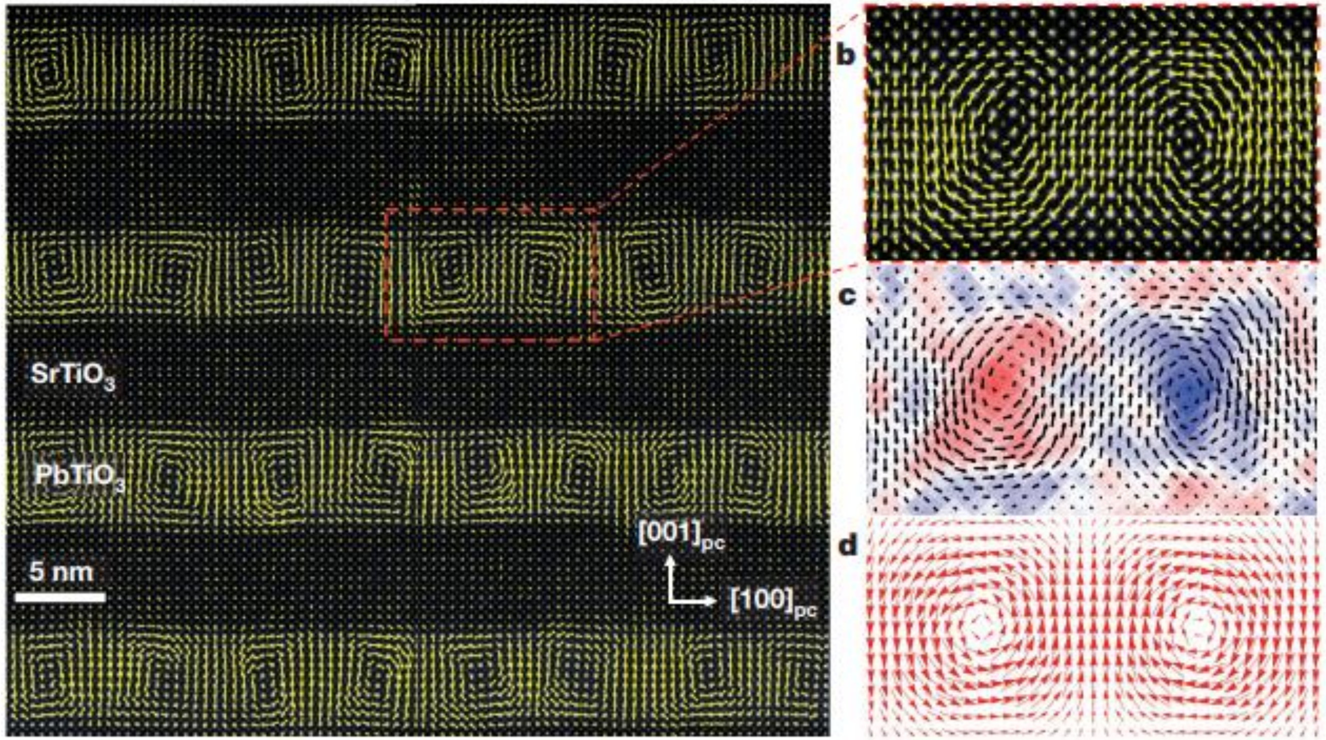


Appl. Phys. Lett. 88, 072905 (2006); https://doi.org/10.1063/1.2172744

Polar Vortices

- Superlattice
- Alternating layers of material

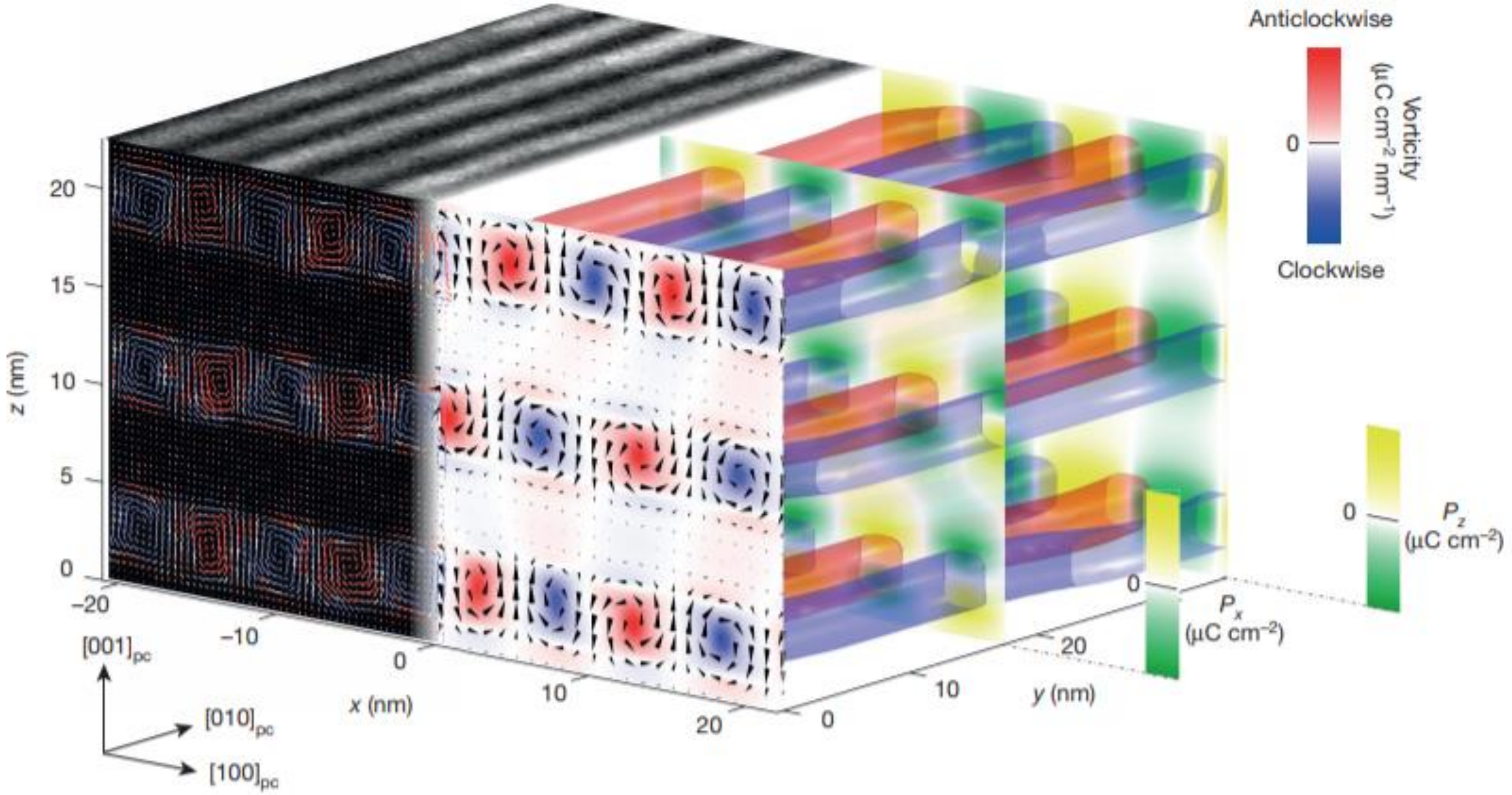




Nature volume530, pages198–201 (11 February 2016) doi:10.1038/nature16463

Polar Vortices

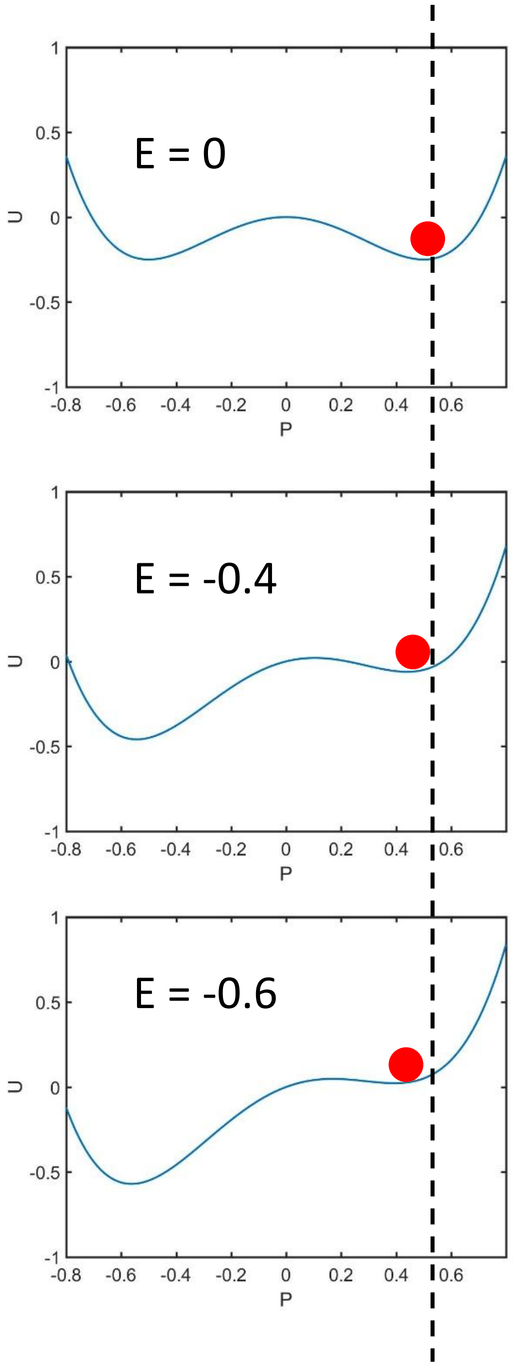
- Phase field simulation vs experimental results
- Superlattice periodicity + energy considerations lead to polar vortex formation

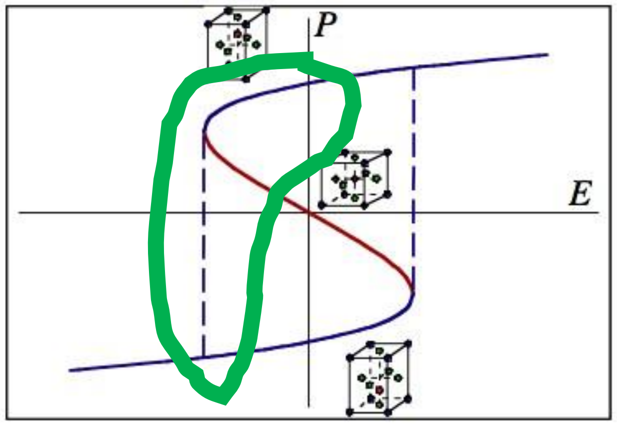


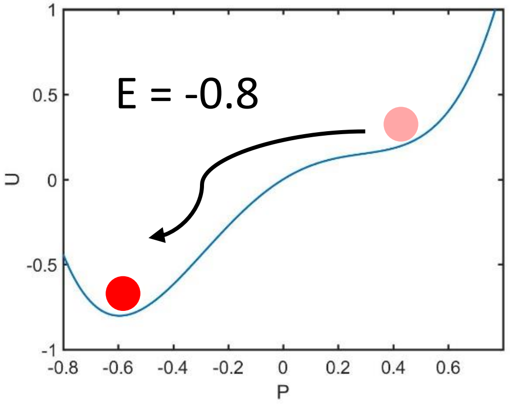
Nature volume530, pages198–201 (11 February 2016) doi:10.1038/nature16463

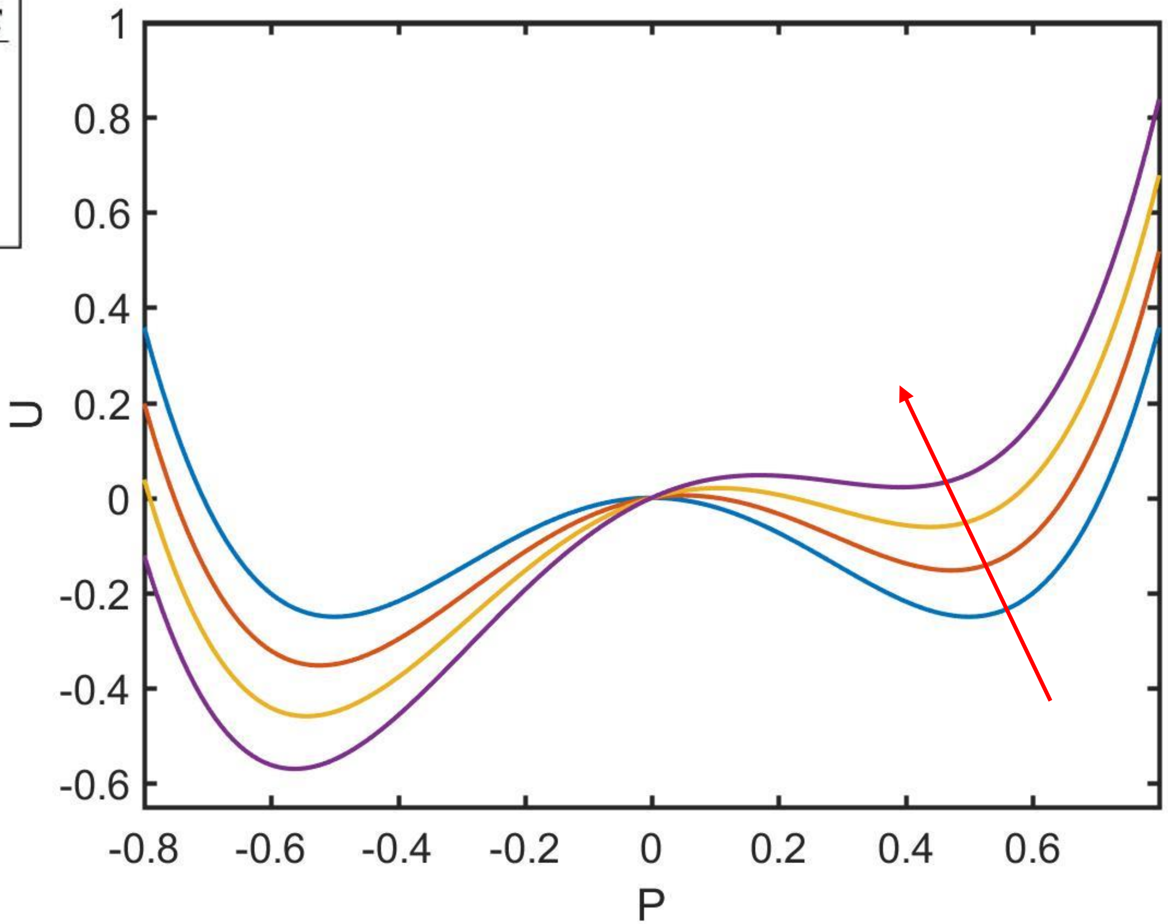
Positive Capacitance

Negative E field
P becomes more negative

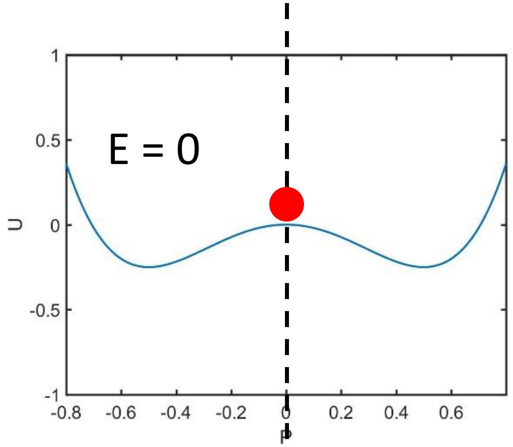


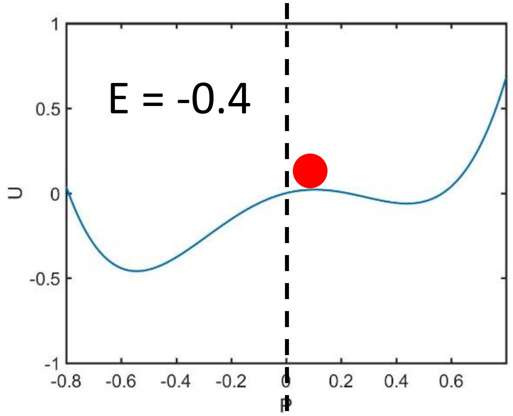


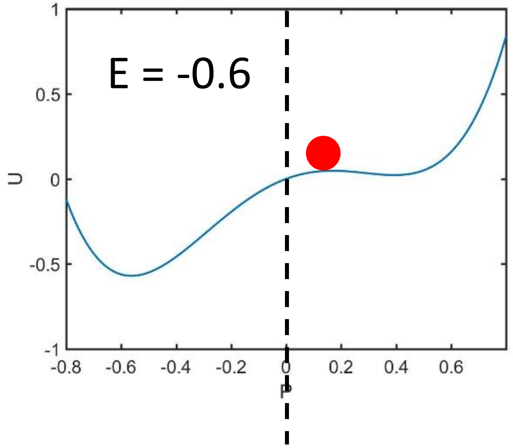




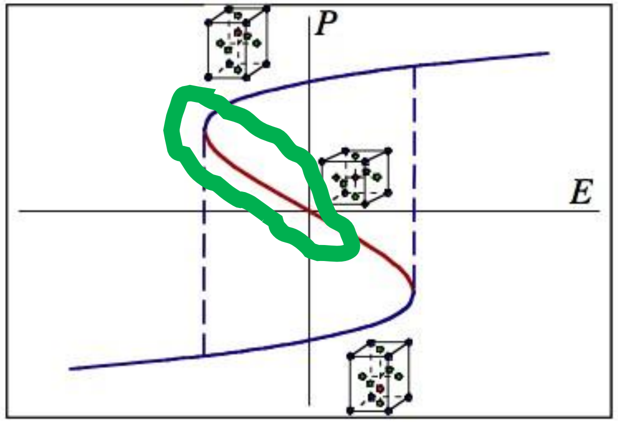
Negative Capacitance!!

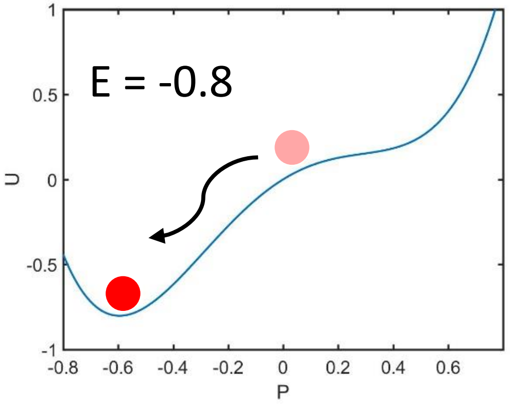






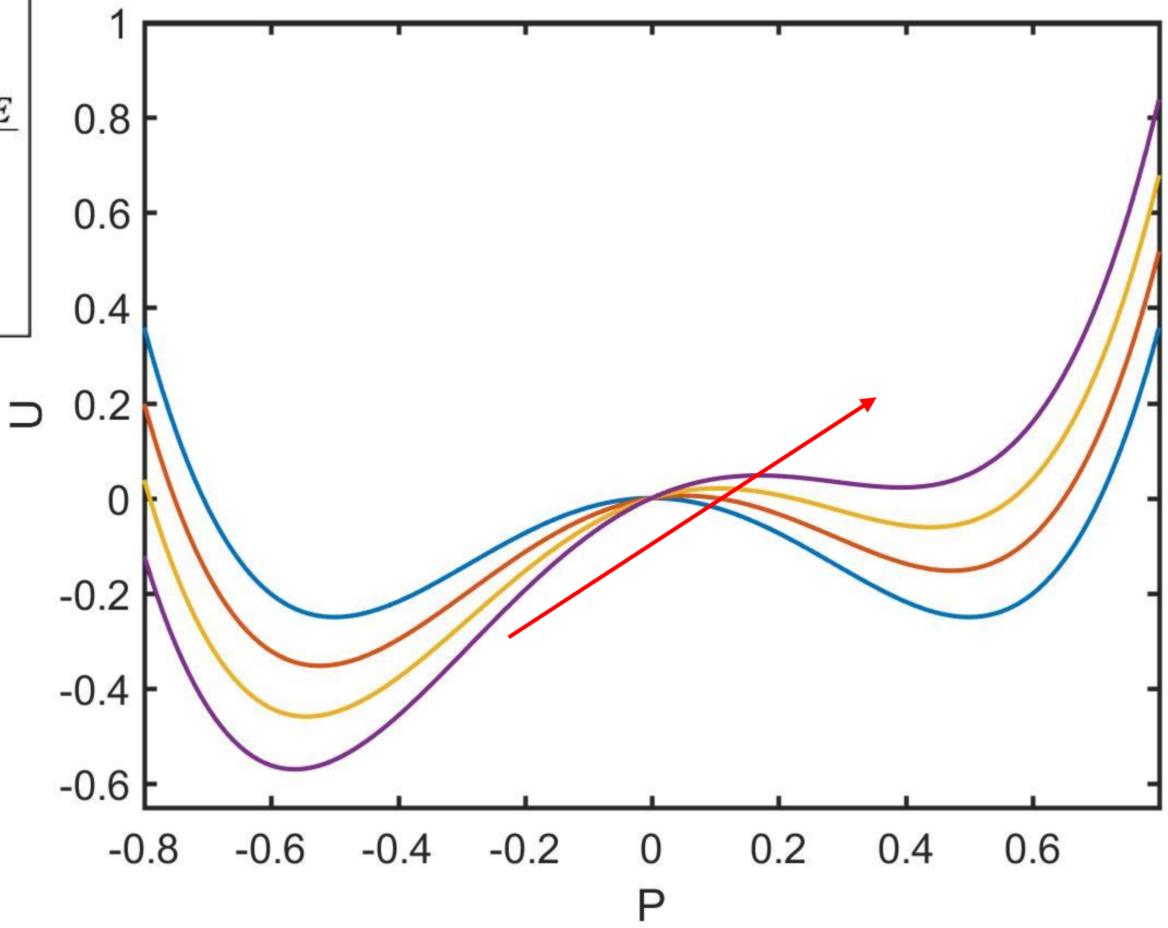
Stabilize metastable state





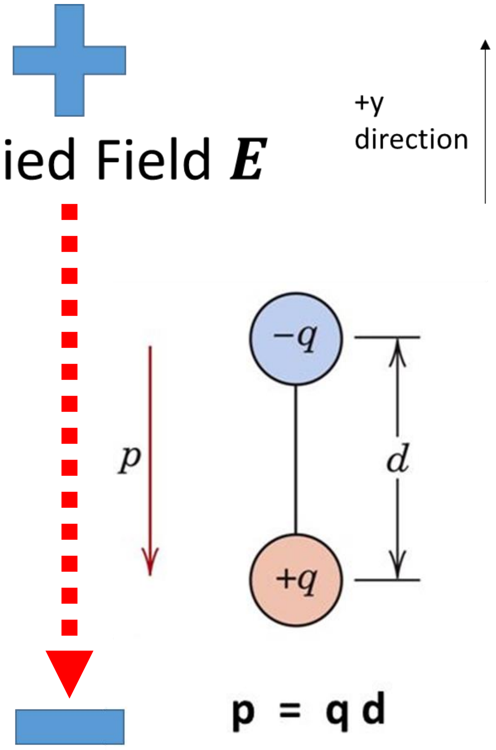
Negative E field

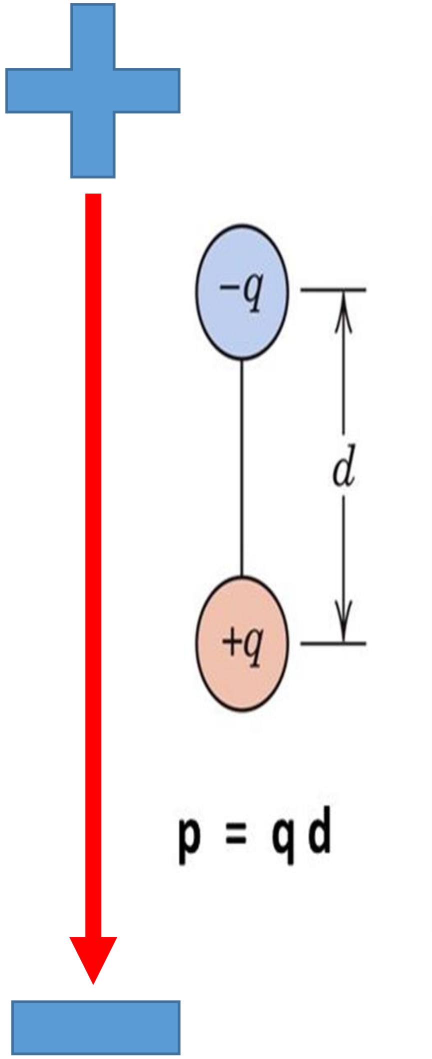
P becomes positive!!!!

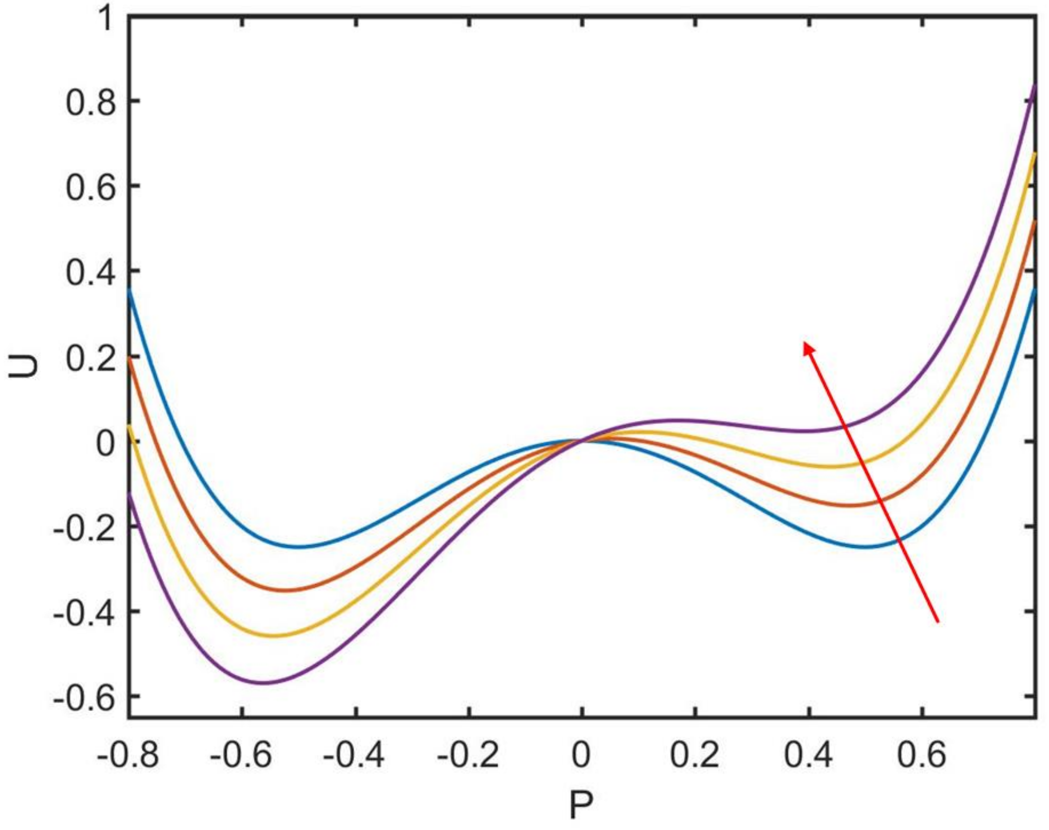


Positive Capacitance

Applied Field $\boldsymbol{E}$

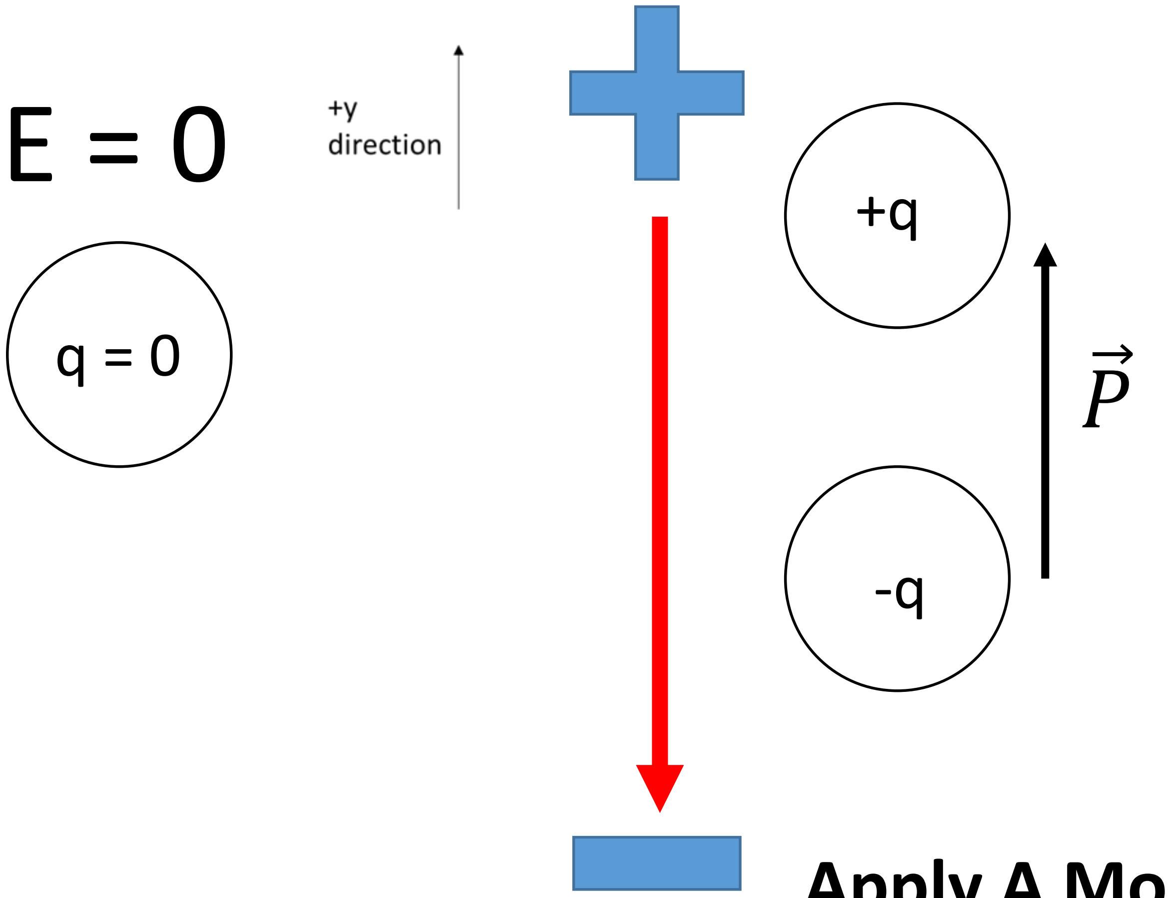


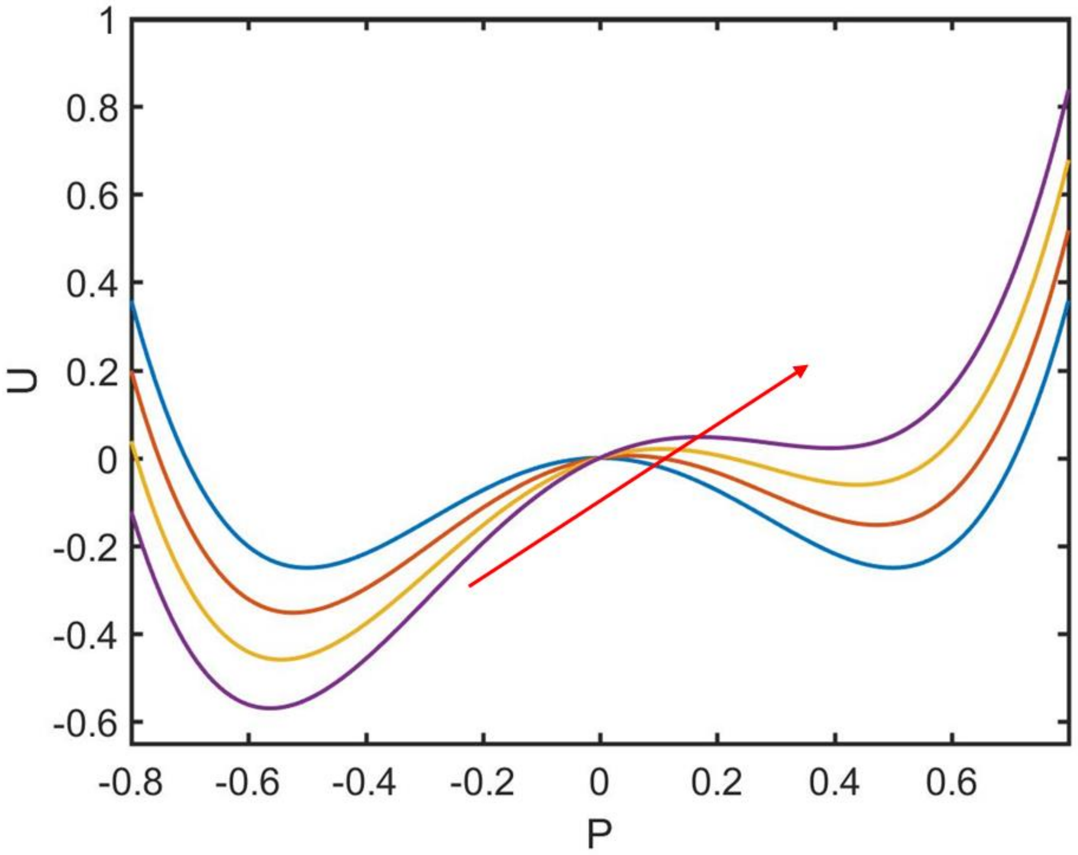




Apply A More Negative E Field

Negative Capacitance

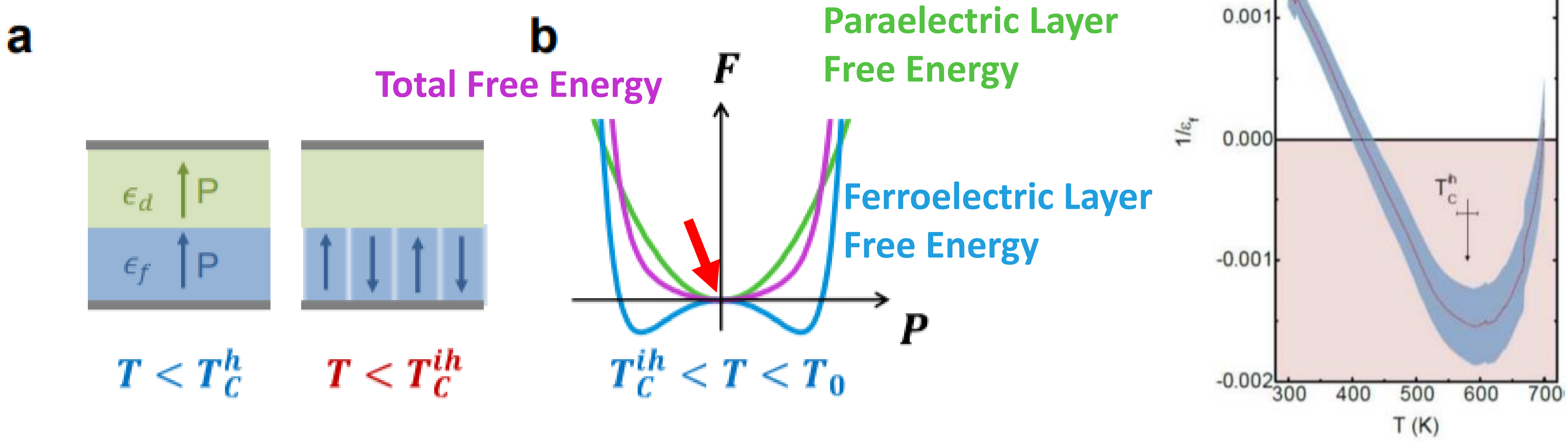




Apply A More Negative E Field

Stabilization of Negative Capacitance

- New era of low power electronics

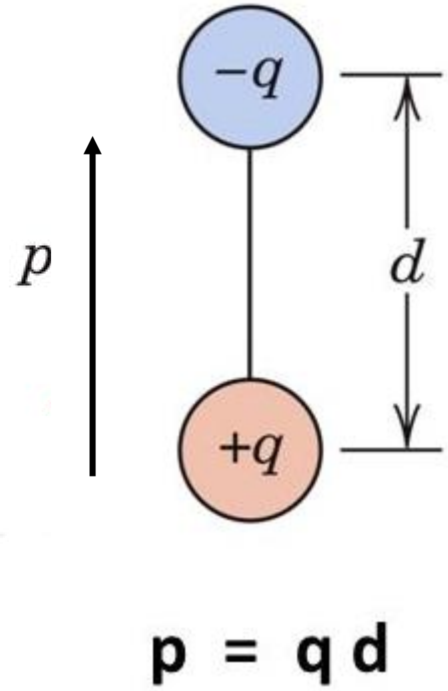


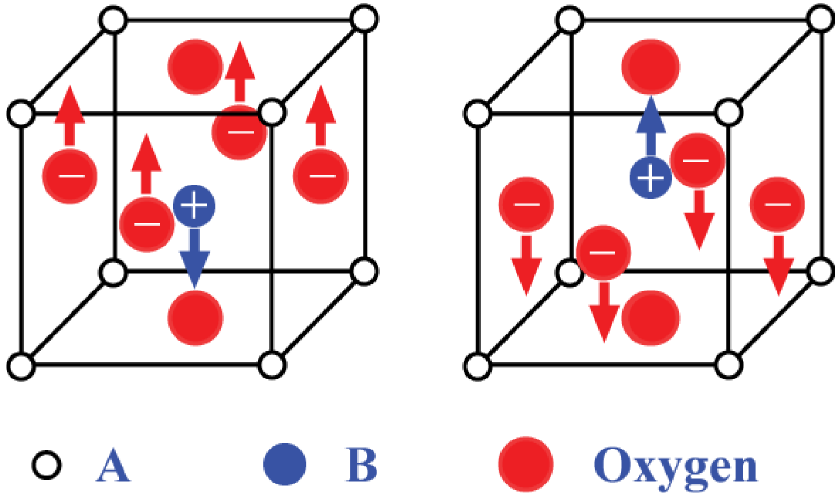
Nature volume 534, pages 524–528 (23 June 2016) doi:10.1038/nature17659

Questions!?

Ferroelectric

- Permanent electric dipole
- $\Psi = \|\vec{P}\|$
- $\vec{P}$ = Polarization vector





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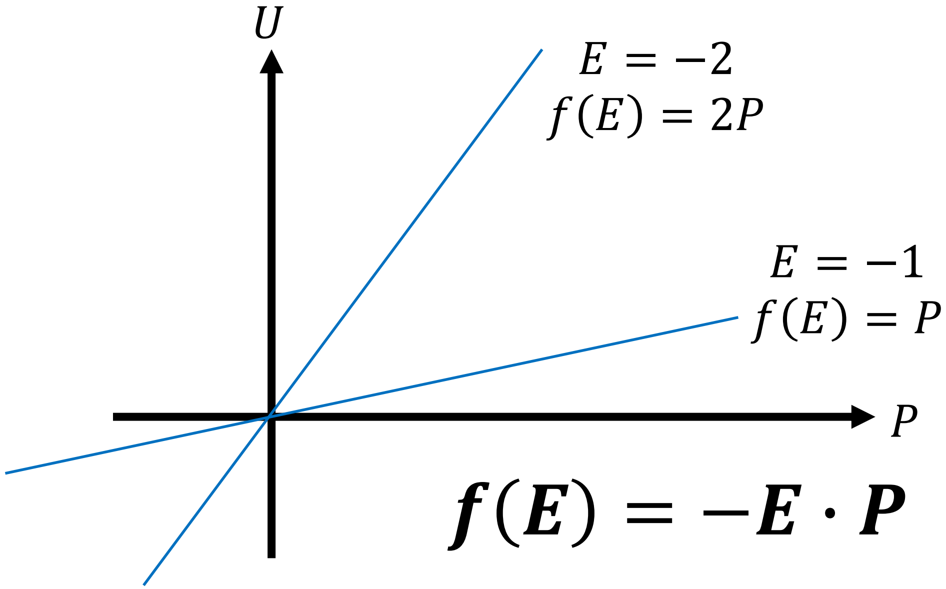
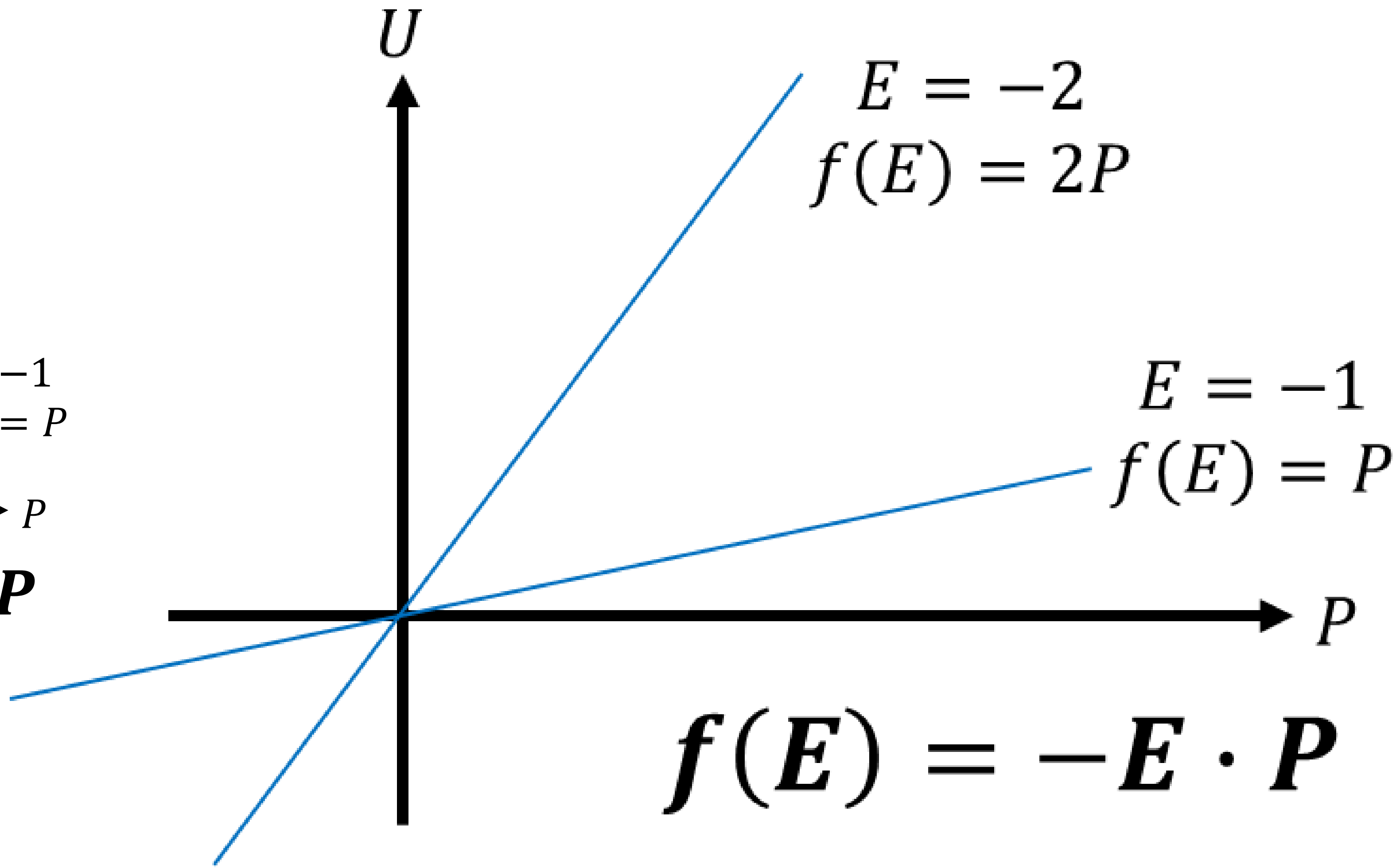

U
P
E = −2
f(E) = 2P
E = −1
f(E) = P
f(E) = −E · P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