Ferroelectricity
Polarization, Capacitance, Dielectric Properties

Capacitance

\[ C = \frac{q}{V} \]

Capacitance of a parallel plate capacitor

\[ C = \varepsilon \varepsilon_0 \frac{A}{L} \]

Relative Dielectric Constant

\[ \varepsilon = \frac{C}{C_{Vac}} \]

Figure 9.16. Two metal plates, separated by a distance, \( L \), can store electric energy after having been charged momentarily by a battery.
Electric Dipole Moment
\[ p = q \cdot x \]

Polarization
\[ P = \frac{p}{V} \equiv \frac{q}{A} \]

Materials *already* possessing permanent dipoles, H$_2$O, BaTiO$_3$, oils, waxes, amorphous polymers,…

Displacement of ions with respect to each other due to external bias, only in ionic materials

Displacement of the e-cloud with respect to the core due to external bias, occurs in ALL dielectric materials

Frequency dependence of the several contributions to the polarizability.

Figure 9.17. An atom is represented by a positively charged core and a surrounding, negatively charged, electron cloud (a) in equilibrium and (b) in an external electric field. (c) Schematic representation of an electric dipole as, for example, created by separation of the negative and positive charges by an electric field, as seen in (b).
Dielectrica, Paraelectrica and Ferroelectrica

Induced dipoles

Permanent dipoles

Permanent dipoles
With spontaneous polarization
Some Important Definitions

\[ D: \text{electrical displacement} \]
\[ \varepsilon: \text{dielectric constant} \]
\[ E: \text{electrical field} \]
\[ E_c: \text{coercive field} \]
\[ d_{ijk}: \text{piezoelectric coefficient (third rank tensor)} \]
\[ p: \text{pyroelectric coefficient} \]
\[ Q_{ijkl}: \text{electrostrictive coefficient (fourth rank tensor)} \]

\[ D = P_s + E \varepsilon \]
Consider Gauss’s Law in the presence of a dielectric:

\[ \nabla \cdot \mathbf{E} = \frac{1}{\varepsilon_0} \rho_{\text{total}} \]

\[ = \frac{1}{\varepsilon_0} \left( \rho_f + \rho_b \right) \]

\( \rho_{\text{total}} \) : Total charge density

\( \rho_f \) : Free charge density

\( \rho_b \) : Bound charge density
\[ \therefore \rho_b = - \nabla \cdot P \]

\[ \therefore \varepsilon_0 \nabla \cdot E = \rho_f - \nabla \cdot P \]

\[ \Rightarrow \nabla \cdot \left( \varepsilon_0 E + P \right) = \rho_f \]

\[ D = \varepsilon_0 E + P \]

**electric displacement** \( D \)

Then,

\[ \nabla \cdot D = \rho_f \]

Integral form:

\[ \oint_{\text{surface}} D \cdot da = Q_{\text{fenc}} \]
Properties

- Spontaneous polarization in the absence applied electrical field.
- Extremely high dielectric constant (~500-15,000).
- Strong non-linear dielectric response to an applied electrical field.
- High strain response to applied electrical field ⇒ piezoelectricity
- Strong variation in polarization with temperature ⇒ pyroelectricity

Perovskite Structure

Typical Perovskite Ferroelectrics

- Pb(Zr,Ti)O₃ - PZT
- Ba(Sr,Ti)O₃ - BST
- KNbO₃ and LiNbO₃
- Pb(Ca,Ti)O₃ - PCT
- Pb(Sr,Ti)O₃ - PST
- Pb(Mg₁/₃Nb₂/₃)O₃ - PbTiO₃
Dielectric Constant: Slope of the $P$ vs. $E$ curve

$$P_i = \varepsilon_0 \varepsilon_{ij} E_j$$

Field dependence of dielectric permittivity $\rightarrow$ Tunability
Ferroelectrica:

Two polarized states of equal energy but opposite direction
Spontaneous Polarization and the Hysteresis
Figure 8. Ferroelectric ($P-E$) hysteresis loop. Circles with arrows represent the polarization state of the material at the indicated fields. The symbols are explained in the text. The actual loop is measured on a (111)-oriented 1.3 μm thick sol-gel Pb(Zr$_{0.45}$Ti$_{0.55}$)O$_3$ film. (Experimental data courtesy of D V Taylor.)
**Free energy** is that portion of energy that is available to perform thermodynamic work; *i.e.*, work mediated by thermal energy.

Most useful to describe properties of solid materials at constant pressure that can expand or shrink as a function of temperature.

\[ F = U - TS \]

Where \( U \) is the internal energy stored in a certain volume

Natural variables: \( T, V, \{N_i\} \)

Differential:

\[ dF = -pdV - SdT + \sum_i \mu_i dN_i \]
Ginzburg Landau Theory of Phase Transitions

Any crystal in thermodynamic equilibrium can be completely specified by the values of a number of variables: Temperature $T$, entropy $S$, electric field $E$, polarization $P$, stress $\sigma$ and strain $s$.

We are applying externally electric fields $E$ and elastic stresses $\sigma$, the crystal responds with the polarization and strain.

Expand the free energy in powers of the dependent variables, with unknown coefficients.

**Simple example:** a single component of the polarization, and ignore the strain field.

$$\mathcal{F}_P = \frac{1}{2} a P^2 + \frac{1}{4} b P^4 + \frac{1}{6} c P^6 + \ldots - EP$$

Finding the minima of $F$:

$$\frac{\partial \mathcal{F}}{\partial P} = 0$$
Paraelectric Materials:

If $a; b; c$ are all positive, the free energy (for $E = 0$) has a minimum at the origin.

$$\frac{\partial F}{\partial P} = aP - E = 0$$

This provides a relationship between the polarizability and the field (in linear response, for small electric field) which defines the dielectric susceptibility

$$\chi = \frac{P}{E} = \frac{1}{a}$$
Ferroelectric Materials:

If $a < 0$, while $b, c > 0$: The free energy will have a double minimum at a finite polarization $P$.

**The ground state has a spontaneous polarization and is a ferroelectric.**

A phase transition happens if $a$ changes continuously with temperature and changes sign at a temperature $T_0$.

Assuming a linear variation of $a(T)$ with temperature: $a_0 \sim (T - T_0)$.

A **second-order**, or **continuous phase transition**. The order parameter (here spontaneous polarization) vanishes continuously at the transition temperature $T_c = T_0$. 

![Diagram of phase transition and spontaneous polarization](image)
If $b < 0$ (while $c$ remains positive).

$T > T_o$ the free energy may have a subsidiary minimum at non-zero $P$.

As $a$ is reduced (temperature lowered), this minimum will drop in energy to below that of the unpolarized state, and will be the thermodynamically favored configuration.

This happens at the Curie temperature $T_c$, which is higher than $T_o$.

At any temperature between $T_c$ and $T_o$ the unpolarized phase exists as a local minimum of the free energy.

The order parameter jumps discontinuously to zero at $T_c$. **First-order or discontinuous transition.**
Why Ferroelectrics?

Wireless Communications
Ferroelectric Memories
Oscillators
Filters

Lead
Oxygen
Titanium

$P$
$E$
$E_C$

$+P_E$
$+P_R$

$-P_R$
$-P_E$

$0$
$1$

or
Temperature Dependence of Spontaneous Polarization

\[ T_C = 490^\circ C \]

\[ P = \left( \frac{\partial D}{\partial T} \right)_E = \frac{\partial P_s}{\partial T} + E \frac{\partial \varepsilon}{\partial T} \]

Pyroelectricity
Why Ferroelectrics?

Exceptional Pyroelectric Response

Pyroelectricity

\[ p = \left( \frac{\partial D}{\partial T} \right)_E = \frac{\partial P_s}{\partial T} + E \frac{\partial \varepsilon}{\partial T} \]
Electrostriction: Coupling between Polarization and Self-Strain
Piezoelectric effect: Strain due to an applied electric field

\[ x_{ij} = d_{kij} E_k \]

Strain due to combined Electrostrictive and Piezoelectric effect

\[ x_{ij} = d_{kij} E_k + Q_{ijkl} P_k P_l \]

\[ = \frac{1}{\varepsilon_0} d_{kij} \varepsilon_{ki}^{-1} P_j + Q_{ijkl} P_k P_l \]

Under non-zero external stress

\[ x_{ij} = d_{kij} E_k + Q_{ijkl} P_k P_l + S_{ijkl} X_{kl} \]
Polarization Switching by an Electric Field

Figure 8. Ferroelectric (P–E) hysteresis loop. Circles with arrows represent the polarization state of the material at the indicated fields. The symbols are explained in the text. The actual loop is measured on a (111)-oriented 1.3 μm thick sol-gel Pb(Zr0.45Ti0.55)O3 film. (Experimental data courtesy of D V Taylor.)
Polarization Switching by an Electric Field

Figure 21  (a) Schematic drawing of atomic displacements on either side of a boundary between domains polarized in opposite directions in a ferroelectric crystal; (b) view of a domain structure, showing 180° boundaries between domains polarized in opposite directions.

Electrical (or 180°-domains) to minimize depolarization.
Applications of Ferroelectrics

✓ Non-Volatile RAMs (memory)
✓ Dynamic RAMs (capacitors)
✓ Tunable Microwave Devices
✓ Pyroelectric Detectors/Sensors
✓ Optical Waveguides
✓ Piezoelectric Sensors/Actuators, MEMS
Non-Volatile RAMs (memory)
Non-Volatile RAMs (memory)

Smart cards use ferroelectric memories. They can hold relatively large amounts of information and do not wear out from use, as magnetic strips do, because they use contactless radio frequency input/output. These cards are the size and shape of credit cards but contain ferroelectric memory that can carry substantial information, such as its bearer's medical history for use by doctors, pharmacists and even paramedics in an emergency. Current smart cards carry about 250 kilobytes of memory.
Tunable Microwave Devices / Optical Waveguides

Dielectric constant \( \varepsilon_{33}/\varepsilon_0 \)

Electric Field, \( E_3 \) [kV/cm]

\[ \Delta \varepsilon \]

\[ \varepsilon(E=0) \]

\[ \text{tunability} = \Phi = \frac{\Delta \varepsilon}{\varepsilon(E = 0)} \]

Filters
Oscillators
Phase shifters
Delay lines
Pyroelectric Detectors/Sensors

Emission of IR

Radiant

\[ \Delta T_r = 1 \text{K} \]

Optical system

Sensor

Heat loss

\[ \Delta T_s = 10^{-2} - 10^{-3} \text{K} \]
Piezoelectric Sensors/Actuators, MEMS