

Materials for Devices: Problem Set 1

1. A capacitor is made of two parallel plates of surface area A and separated by a distance L . It supports a charge Q on each plate (positive on one and negative on the other) and an associated voltage difference V across the plates. The capacitance C of the capacitor is defined as:

$$C = \frac{Q}{V}.$$

For a parallel plate capacitor, the charge density $\sigma = \frac{Q}{A}$ on each plate is related to the displacement field of the dielectric material between the plates through:

$$\sigma = |\mathbf{D}|.$$

- (i) Show that:

$$C = \varepsilon \frac{A}{L},$$

where ε is the permittivity of the dielectric material between the parallel plates.

- (ii) What is the capacitance of an *empty* parallel plate capacitor with plates of surface area 500 mm^2 and separated by 2.5 mm ? If a potential difference of 10 V is applied across the plates, what is the magnitude of the charge stored on each plate? And the surface charge density?
- (iii) Consider the insertion of SiO_2 ($\kappa = 4.52$) between the plates. For the same applied potential difference of 10 V , calculate the capacitance, the magnitude of charge stored on each plate, and the surface charge density.
- (iv) What is the polarisation of SiO_2 in the setup above? Relate this polarisation to the free charge that is present in an empty parallel plate capacitor.
- (v) What would be the surface area of a new capacitor of the same capacitance and thickness as the SiO_2 capacitor above, but made from a ferroelectric material with a dielectric constant one hundred times greater than that of SiO_2 ?

Solution

- (i) From electrostatics, the electric field across a parallel plate capacitor is constant and related to the voltage difference as $V = L|\mathbf{E}|$. Using this expression for the voltage, together with the relation between charge and charge density, we obtain:

$$C = \frac{Q}{V} = \frac{\sigma A}{L|\mathbf{E}|}.$$

By definition, $|\mathbf{D}| = \varepsilon|\mathbf{E}|$, and for a parallel plate capacitor we also have $\sigma = |\mathbf{D}|$, so that we obtain:

$$C = \frac{\sigma A}{L \frac{\mathbf{D}}{\varepsilon}} = \varepsilon \frac{\sigma A}{L\sigma} = \varepsilon \frac{A}{L}.$$

This result implies that the capacitance of a parallel plate capacitor only depends on the geometry of the capacitor and on the dielectric material between the conducting plates.

- (ii) For an empty parallel plate capacitor, we have the permittivity of free space ϵ_0 , and obtain the following capacitance in SI units:

$$C = \epsilon_0 \frac{A}{L} = 8.854 \times 10^{-12} \times \frac{5 \times 10^{-4}}{2.5 \times 10^{-3}} = 1.77 \times 10^{-12} \text{ F.}$$

For an applied potential difference of 10 V, we obtain a stored charged equal to:

$$Q = CV = 1.77 \times 10^{-12} \times 10 = 1.77 \times 10^{-11} \text{ C.}$$

The resulting surface charge density is:

$$\sigma = \frac{Q}{A} = \frac{1.77 \times 10^{-11}}{5 \times 10^{-4}} = 3.54 \times 10^{-8} \text{ Cm}^{-2}.$$

- (iii) The dielectric constant κ is related to the permittivity by $\kappa = \frac{\epsilon}{\epsilon_0}$. Let us label quantities associated with an empty parallel plate capacitor with a zero subindex and quantities associated with the same capacitor with a dielectric as usual. We obtain:

$$\begin{aligned} C &= \epsilon \frac{A}{L} = \frac{\epsilon}{\epsilon_0} \epsilon_0 \frac{A}{L} = \kappa C_0, \\ Q &= CV = \kappa C_0 V = \kappa Q_0, \\ \sigma &= \frac{Q}{A} = \frac{\kappa Q_0}{A} = \kappa \sigma_0. \end{aligned}$$

Inserting SiO_2 with $\kappa = 4.52$ as the dielectric, we obtain:

$$\begin{aligned} C &= \kappa C_0 = 4.52 \times 1.77 \times 10^{-12} = 8.00 \times 10^{-12} \text{ F}, \\ Q &= \kappa Q_0 = 4.52 \times 1.77 \times 10^{-11} = 8.00 \times 10^{-11} \text{ C}, \\ \sigma &= \kappa \sigma_0 = 4.52 \times 3.54 \times 10^{-8} = 1.60 \times 10^{-7} \text{ Cm}^{-2}. \end{aligned}$$

- (iv) The magnitude of the polarisation is given by $|\mathbf{P}| = \epsilon_0 |\mathbf{E}| (\kappa - 1)$, and relating the electric field magnitude to the potential difference through $|\mathbf{E}| = \frac{V}{L}$, we obtain:

$$|\mathbf{P}| = \epsilon_0 \frac{V}{L} (\kappa - 1) = 8.854 \times 10^{-12} \times \frac{10}{2.5 \times 10^{-3}} \times (4.52 - 1) = 1.25 \times 10^{-7} \text{ Cm}^{-2}.$$

For a parallel plate capacitor, the total charge density is related to the displacement field magnitude as $\sigma = |\mathbf{D}|$. In turn, the displacement field is $\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$, so that the total charge density can be expressed as:

$$\sigma = \epsilon_0 \mathbf{E} + \mathbf{P}.$$

The first term provides an empty parallel plate capacitor contribution coming from the free charge on the plates, and the second term quantities the changes induced by the polarisation.

- (v) Let the permittivity of SiO_2 be ϵ_{SiO_2} and that of a ferroelectric material be $\epsilon_{\text{ferro}} = 100\epsilon_{\text{SiO}_2}$. The surface area A_{ferro} associated with the new setup can be related to the original surface area A_{SiO_2} through:

$$A_{\text{ferro}} = \frac{CL}{\epsilon_{\text{ferro}}} = \frac{CL}{100\epsilon_{\text{SiO}_2}} = 10^{-2} A_{\text{SiO}_2}.$$

Therefore, the new surface area is $10^{-2} \times 5 \times 10^{-4} = 5 \times 10^{-6} \text{ m}^2$.

2. A ceramic material has a piezoelectric coefficient of 250 pCN^{-1} and a dielectric constant of 500. A compressive stress of 5 MPa is applied across a 1 cm thick sample of the material. Calculate the voltage that will develop across the sample.

Solution

The voltage associated with a piezoelectric sample of rectangular prismatic shape is $\Delta V = \frac{dT L}{\varepsilon}$, where d is the piezoelectric coefficient, T is the stress, L is the thickness, and ε is the dielectric constant. Direct substitution of the values provided, using SI units, gives:

$$\Delta V = \frac{250 \times 10^{-12} \times 5 \times 10^6 \times 10^{-2}}{500 \times 8.854 \times 10^{-12}} = 2.82 \times 10^3 \text{ V.}$$

3. Goldschmidt postulated that materials that adopt the perovskite structure arrange so that “the number of anions surrounding a cation tends to be as large as possible, subject to the condition that all anions touch the cation”. In this problem, we use this principle to derive the Goldschmidt tolerance factor.

- (i) Sketch a unit cell of a cubic perovskite ABX_3 structure, placing the B cation at the centre of the cell.
- (ii) Let the lattice parameter of the cubic cell be a . Show that according to Goldschmidt’s statement above, then:

$$a = 2(r_B + r_X),$$

where r_B and r_X are the ionic radii of ions B and X , respectively.

- (iii) Show that according to Goldschmidt’s statement above, then:

$$\sqrt{2}a = 2(r_A + r_X),$$

where r_A and r_X are the ionic radii of ions A and X , respectively.

- (iv) Therefore, show that for an ideal cubic perovskite, the Goldschmidt tolerance factor:

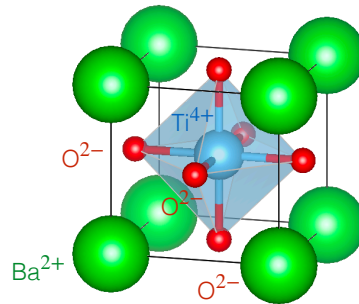
$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)},$$

is equal to 1.

- (v) For $BaTiO_3$, the ionic radii are $r_{Ba^{2+}} = 1.75 \text{ \AA}$, $r_{Ti^{4+}} = 0.75 \text{ \AA}$, and $r_{O^{2-}} = 1.21 \text{ \AA}$. Calculate the Goldschmidt tolerance factor for $BaTiO_3$ and discuss the result in terms of the stability of cubic $BaTiO_3$.

Solution

- (i) As an example, we consider the cubic perovskite phase of $BaTiO_3$:



- (ii) A straight line joining oxygens (X) at opposite faces of the cube and passing through the central titanium (B) has length a . This line crosses a full O atom (half from each side) and a full Ti atom, and according to Goldsmith’s statement it gives:

$$a = 2(r_B + r_X).$$

- (iii) A straight line joining barium (A) atoms at diagonally opposite corners of a face of the cube and passing through an oxygen (X) at the centre of the face has length $\sqrt{2}a$. This line crosses a full O atom and a full Ba atom (half on each corner), and according to Goldschmidt’s statement it gives:

$$\sqrt{2}a = 2(r_A + r_X).$$

(iv) Considering the two conditions for ideal packing for a cubic perovskite, we have:

$$\begin{cases} a = 2(r_B + r_X) \\ \sqrt{2}a = 2(r_A + r_X) \end{cases}$$

Removing a from these two equations leads to $r_A + r_X = \sqrt{2}(r_B + r_X)$ for an ideal cubic perovskite. Therefore, the tolerance factor $t = 1$.

(v) The Goldschmidt tolerance factor for BaTiO_3 reads:

$$t = \frac{r_{\text{Ba}^{2+}} + r_{\text{O}^{2-}}}{\sqrt{2}(r_{\text{Ti}^{4+}} + r_{\text{O}^{2-}})} = \frac{1.75 + 1.21}{\sqrt{2}(0.75 + 1.21)} = 1.07.$$

This factor is larger than 1, indicating that the Ba^{2+} cations are too large for ideal packing. As a result, the BaTiO_3 structure is larger than ideal to be able to accommodate the Ba^{2+} cations, leaving empty space around the comparatively smaller Ti^{4+} cations. This leads to the Ti^{4+} cations being relatively free to move from their ideal position at the centre of the octahedron, driving distortions from the ideal cubic phase in BaTiO_3 .

4. Consider a ferroelectric material whose free energy is given by:

$$\mathcal{F}(P, T) = a(T - T_c)P^2 + \frac{b}{2}P^4,$$

where P is the polarisation, T the temperature, and a , b , and T_c are positive scalar parameters. This free energy provides a universal characterisation of ferroelectric-to-paraelectric phase transitions.

- (i) Find the extrema of the free energy with respect to P in the case when $T > T_c$ and sketch the resulting function.
- (ii) Find the extrema of the free energy with respect to P in the case when $T < T_c$ and sketch the resulting function.
- (iii) Calculate the polarisation P as a function of temperature T . What is the role of T_c ?

Solution

- (i) The extrema of a function are given by the points at which its first derivative vanishes. In our case, the derivative of the free energy with respect to polarisation is:

$$\frac{\partial \mathcal{F}}{\partial P} = \frac{\partial}{\partial P} \left(a(T - T_c)P^2 + \frac{b}{2}P^4 \right) = 2a(T - T_c)P + 2bP^3.$$

Therefore, the condition for extrema of the free energy with respect to polarisation is:

$$2a(T - T_c)P + 2bP^3 = 0.$$

This equation has two possible solutions:

$$\begin{cases} P = 0 \\ P^2 = -\frac{a}{b}(T - T_c) \end{cases}$$

For $T > T_c$, the second solution is not a physically valid solution as the right hand side becomes negative. Therefore, the only solution in this case is $P = 0$.

To establish the nature of this extremum, we can evaluate the second derivative:

$$\frac{\partial^2 \mathcal{F}}{\partial P^2} = \frac{\partial}{\partial P} (2a(T - T_c)P + 2bP^3) = 2a(T - T_c) + 6bP^2.$$

At the extremum, we get:

$$\left. \frac{\partial^2 \mathcal{F}}{\partial P^2} \right|_{P=0} = 2a(T - T_c) > 0.$$

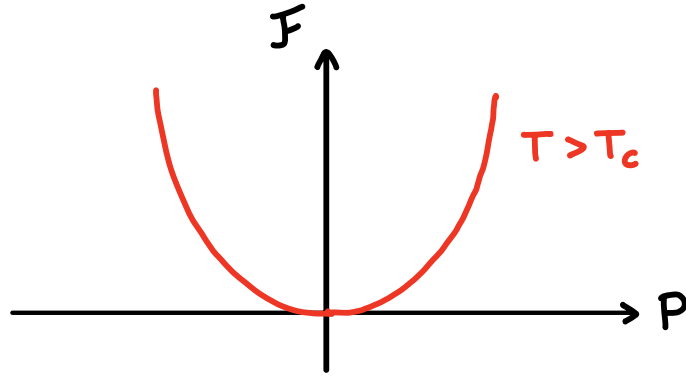
Therefore, the extremum is a minimum. The resulting sketch of the free energy for $T > T_c$ is shown in the Figure below. The free energy has a single minimum corresponding to $P = 0$, indicating that it is describing the high temperature non-polar phase.

- (ii) For $T < T_c$, all solutions are now physically valid:

$$\begin{cases} P = 0 \\ P^2 = -\frac{a}{b}(T - T_c) \implies P = \pm \sqrt{-\frac{a}{b}(T - T_c)} \end{cases}$$

and we end up with three extrema. To determine their nature, we now get:

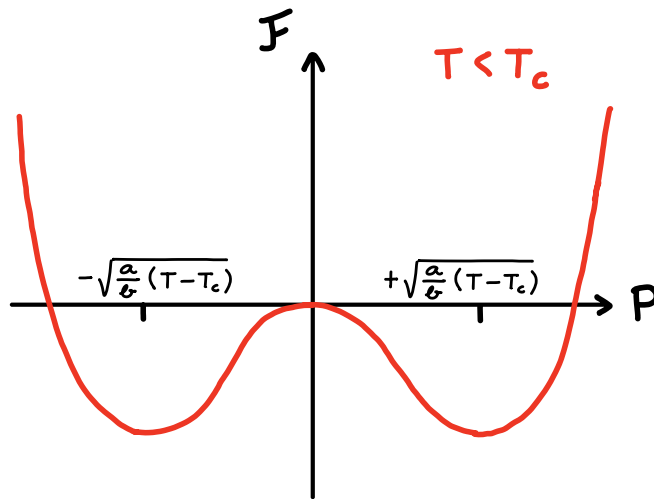
$$\left. \frac{\partial^2 \mathcal{F}}{\partial P^2} \right|_{P=0} = 2a(T - T_c) < 0,$$



which corresponds to a maximum; and:

$$\begin{aligned} \frac{\partial^2 \mathcal{F}}{\partial P^2} \Big|_{P=\pm\sqrt{-\frac{a}{b}(T-T_c)}} &= 2a(T - T_c) + 6b \left(-\frac{a}{b}(T - T_c) \right) \\ &= 2a(T - T_c) - 6a(T - T_c) \\ &= -4a(T - T_c) > 0, \end{aligned}$$

which correspond to minima. The resulting sketch of the free energy for $T < T_c$ is shown in the Figure below. The free energy has two minima corresponding to polarizations of non-zero magnitude of opposite signs. This free energy describes the low temperature polar phases.



(iii) The polarisation is given by:

$$P = \begin{cases} 0 & \text{for } T > T_c, \\ \pm\sqrt{-\frac{a}{b}(T - T_c)} & \text{for } T < T_c. \end{cases}$$

The Figure below shows a sketch of the polarisation as a function of temperature, clearly highlighting how T_c is the transition temperature marking the ferroelectric-to-paraelectric boundary.

