HW#1 Solutions

1) Silicon capacitor: The potential energy can be expressed as

$$U=\frac{V}{2}\varepsilon_0 E_0^{\,2}+\int_0^{E_{in}} \vec{E}'_{in}\, d\left(\vec{P}'\cdot V\right)$$

where V is the sample volume, E_0 is the magnitude of the field that would exist in the absence of the solid, and E' and P' are the dummy electric-field and polarization vector variables. Since the solid is inside a metallic parallel-plate capacitor (i.e., a Si sample with metal plates on the surface), $\vec{E}_0 = \vec{E}_{in}$. Furthermore, we can assume that $\vec{E}_{in}$ and $\vec{P}_{in}$ are both uniform so that $d\left(\vec{P}_e\cdot V\right) = V\cdot d\vec{P}_e$. And if we consider Si as a good dielectric, $\vec{P}_e \approx \varepsilon_0\chi_e\vec{E}_{in}$ so that

$$U'=\frac{U}{V}=\frac{1}{2}\varepsilon_0 E_{in}^{\,2}+\varepsilon_0\chi_e\int_0^{E_{in}} \vec{E}'_{in}\cdot d\vec{E}'_{in} = \frac{1}{2}\varepsilon_0 E_{in}^{\,2}\left(1+\chi_e\right)=\frac{1}{2}\varepsilon_0\varepsilon_r E_{in}^{\,2}$$

a) The maximum U' occurs when $\boldsymbol{E}_{in} = \boldsymbol{E}_{\max}$, so that

$$\left[U'\right]^{\max} = 4.8\times10^{4}\ J/m^3 = 4.8\times10^{-2}\ J/cm^3 \quad \text{for } \varepsilon = 12,\ E_{max} = 3\text{x}10^7\ \text{V/cm}$$

b) The maximum polarization per unit volume is simply

$$P_e^{max}=\varepsilon_0\chi_e E_{max}=2.9\times10^{-3}\ \text{Cb}/\text{m}^2 \quad \text{for } \chi_e=\varepsilon_r - 1 = 11$$

2) Polarizability of conducting sphere

By definition, $\vec{p} = \alpha\vec{E}_{local}$, where $\vec{p}\rightarrow dipole\ \ moment,\ \ \alpha\rightarrow polarizability$.

In this case: $\vec{E}_{local} = \vec{E}_0$ (applied field). From geometrical effects, we know that a "depolarization" field inside a sphere is given by:

$$\vec{E}_{in} = \vec{E}_0 - \frac{\vec{P}}{3\varepsilon_0}$$

But by definition, $\mathbf{P} = n\mathbf{p} = \mathbf{p}/V = \mathbf{p}/[(4/3)\pi a^3]$. And by shielding effects, $\vec{\boldsymbol{E}}_{in} = 0$. So,

$$\vec{\boldsymbol{E}}_0 = \frac{\vec{\boldsymbol{p}}}{3\boldsymbol{\varepsilon}_0} = \frac{\vec{\boldsymbol{p}}}{4\pi\boldsymbol{\varepsilon}_0 a^3} = \frac{\alpha\vec{\boldsymbol{E}}_0}{4\pi\boldsymbol{\varepsilon}_0 a^3} \Rightarrow \alpha = 4\pi\boldsymbol{\varepsilon}_0 a^3$$

3. Atomic polarizability: Diamond, silicon, and germanium

(a)	Si	Ge	C (diamond)
ε_r	11.7	15.8	5.5
Atomic concentration [m^{-3}]	5.00E+28	4.42E+28	1.76E+29

(b)	Si	Ge	C (diamond)
$(\varepsilon_r-1)/(\varepsilon_r+2)$	7.81E-01	8.31E-01	6.00E-01
Polarizability, [Cb-m^2/V]	4.147E-40	4.994E-40	9.051E-41

(c)	Si	Ge	C (diamond)
atomic radius [A]			
$R = (\alpha/4\pi\varepsilon_0)^{1/3}$	1.55	1.65	0.93

(d)	Si	Ge	C (diamond)
Nearest neighbor distance [Ang], R_{nn}	2.35	2.45	1.54
Half nearest neighbor distance, $R_{nn}/2$	1.18	1.23	0.77
$R_{nn}/(2R_0)$	0.76	0.74	0.82

4. (Ionic polarizability): KI and MgO

(a)	KI	MgO
Nearest neighbor separation [Ang]	3.533	2.1
Unit cell constant [Ang]	7.066	4.2
Unit cell volume [m^3]	3.52794E-28	7.4088E-29
Stiffness coeff C11 [N/m^2]	2.740E+10	2.860E+11

(b)	KI	MgO
Density [KG/m^3]	3142.95	3634.02
Speed of sound [m/s]	2952.61	8871.34
q/e	1	2
α	2.65E-39	1.71E-39

Note in (b) that MgO is bivalent, i.e., each ion is doubly charged

(c)	KI	MgO
χ_e ($\approx n^*\alpha/\varepsilon_0$)	3.40	10.4
Calculated εr	4.40	11.4
*Accepted εr	5.10	9.65

www.crystran.co.uk/kidata.htm*

5) Ferroelectric Linear Array

From the dipole-pair analysis in the text, w expect ferroelectricity to be possible only when dipoles are co-linear, as shown for a linear array in Fig. 1.

Field at nth atom from n-1 dipole $\vec{E}_{n,n-1} = \frac{2\boldsymbol{p}}{a^3}(-\hat{x})$

Field at nth atom from n-2 dipole $\vec{E}_{n,n-2} = \frac{2\boldsymbol{p}}{(2a)^3}(-\hat{x})$

Field at nth atom from n+1 dipole $\vec{E}_{n,n+1} = \frac{2\boldsymbol{p}}{(a)^3}(-\hat{x})$

Field at nth atom from n+2 dipole $\vec{E}_{n,n+2} = \frac{2\boldsymbol{p}}{(2a)^3}(-\hat{x})$

So by superposition, the total field at the nth atom is:

$$\vec{E}_{total} = \left(\frac{2\boldsymbol{p}}{a^3}+\frac{2\boldsymbol{p}}{(2a)^3}+..+\frac{2\boldsymbol{p}}{a^3}+\frac{2\boldsymbol{p}}{(2a)^3}+...\right)(-\hat{x})$$

or equivalently,

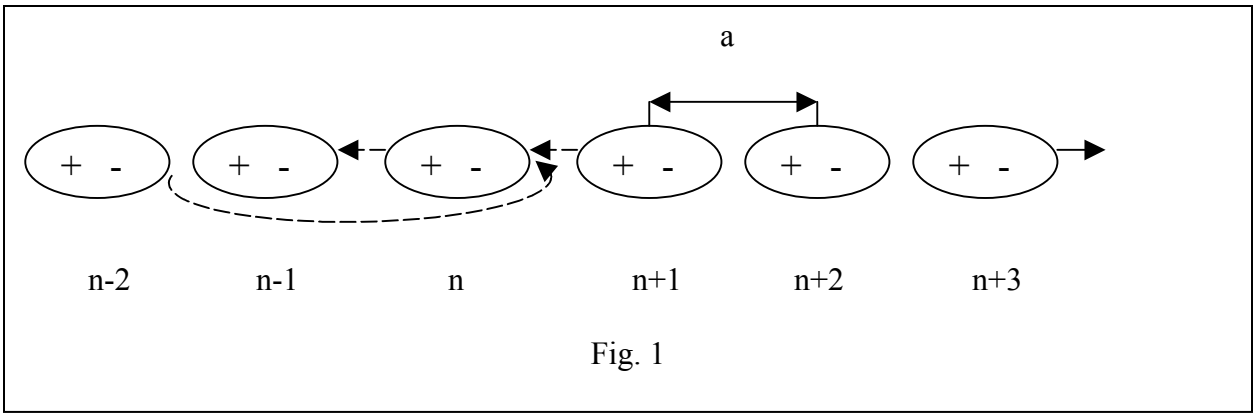

Fig. 1

$$\vec{E}_{total} = \frac{4p}{a^3}\sum_{n=1}^{N}\frac{1}{n^3}(-\hat{x})$$

This field at the nth atom induces a dipole $\vec{p}_n = \alpha\vec{E}_{total} = \frac{4\alpha p}{a^3}\sum_{n=1}^{N}\frac{1}{n^3}(-\hat{x})$. But the ferroelectric threshold occurs when this dipole moment equals the moments of all other atomic dipoles – the self-consistency criterion. This is stated mathematically as

$$\left|\vec{p}_n\right| = p = \frac{4\alpha p}{a^3}\sum_{n=1}^{N}\frac{1}{n^3} \qquad \text{or} \qquad \alpha = \frac{a^3}{4\sum_{n=1}^{N}\frac{1}{n^3}}$$

where N is half the number of atoms in the line (to not overcount)

6. (Temperature-dependence of ferroelectrics for $T < T_C$: Pyroelectricity)

(a) For $P_e = P_s\,(1\text{-}T/T_C)^{1/2}$, the pyroelectric coefficient is $|dP_e/dT| = P_S\,(1 - T/T_C)^{-1/2}/(2T_C)$. For $LiTaO_3$, we have (from Kittel) $T_C = 938$ K, and $P_S = 50\text{x}10^{-2}$ Cb/m^2. So $|dPe/dT| = 3.3\text{x}10^{-5}$ Cb/m^2-K.

(b) For TGS, we have can find numerous references on the www, for example, www.girnet.com/tgs_dtgs.htm. Although there is clearly some variation, a typical value is $P_S = 2.8\text{x}10^{-2}$ Cb/m^2 and $T_C = 322$ K. So at 320 K, we find $|dPe/dT| = 5.5\text{x}10^{-4}$ Cb/m^2-K. This about 17 times higher than $|dPe/dT|$ for $LiTaO_3$ at the same temperature. Clearly the reason is the close proximity to the Curie temperature T_C for TGS, which causes the factor $(1 - T/T_C)^{1/2}$ in the denominator to get quite small.

7. (Temperature-dependence of ferroelectrics for $T > T_C$: Curie-Weiss Law)

a. The ferroelectric criterion allows us to write $n\alpha/3\varepsilon_0 = 1$, or $n\alpha = 3\varepsilon_0$ at $T = T_C$. If the temperature is raised just above $T = T_C$, we assume that the ferroelectricity will be broken by the movement of the Ti atom due to thermal expansion. So we Taylor expand $n\alpha$ as a function of T about $T = T_C$, keeping in mind that $\alpha = p/E = qd/E$ where q is the charge on each dipole, d is the separation of the charge, and E is the local electric field: $n\alpha = n\alpha\,|_{T=TC} - [\partial\,(n\alpha)/\partial T]\,|_{T=TC}\cdot(T\text{-}T_C)$, where the minus sign in front of the second term is added to make sure the $n\alpha$ product decreases above T_C, consistent with the paraelectric behavior that occurs there. But $\partial(n\alpha)/\partial T \approx n\partial\alpha/\partial T = n\partial(p/E)/\partial T = (nq/E)\,\partial d/\partial T = (nqd/E)A(1/3)\beta = (P/E)$

$A(1/3)\beta = (\chi_e\varepsilon_0)\cdot A(1/3)\beta$, where d is the effective dipole length, β is the volume expansivity ($\equiv 1/V)(\partial V/\partial T$), the 1/3 factor relates linear expansion to volumetric expansion, and A is a unitless fitting parameter that relates the expansion of the dipole to the expansion of the lattice. So we have

$$n\alpha = 3\varepsilon_0 - (\chi_e\varepsilon_0)\cdot A\beta/3\,|_{T=TC}\cdot(T-T_C)$$

By substituting this into the feedback form of the Clausius-Mosotti relation for ε_r we get

$$\varepsilon_r - 1 = \chi_e = \frac{n\alpha/\varepsilon_0}{1-n\alpha/3\varepsilon_0} = \frac{3+\chi_e\cdot A\beta/3|_{T=Tc}\cdot(T-T_C)}{1-\left[1-(\chi_e A\beta/3)|_{T=Tc}\,(T-T_C)/3\right]} \approx \frac{27}{(\chi_e A\beta)|_{T=Tc}\,(T-T_C)}$$

where the second term in the numerator is dropped assuming $\chi_e A\beta/3 << (T-T_C)^{-1}$. Clearly, the resulting expression diverges at $T = T_C$, which is physically unallowed since it brings the possibility of infinite electrostatic energy, $(1/2)\varepsilon_r(E_{in})^2$. So we must add to the denominator a unitless constant term B which is determined uniquely by the condition that χ_e equals the experimental value at $T = T_C$. That is

$$\chi_e \approx \frac{27}{B+(\chi_e A\beta)|_{T=Tc}\,(T-T_C)} \qquad (1)$$

From at least one source in the literature,[1] one finds that $\varepsilon_r \approx 5000$ at $T = T_C$, so that $A = 27/5000 = 5.4\text{x}10^{-3}$.

b. From materials tables we have $\beta \approx 30\text{x}10^{-6}$ /K for $BaTiO_3$ between 300 and 400 K.[2] To estimate A, we plot Eqn (1) with A treated parametrically, as shown in Fig. 1. The value A = 0.002 yields the best agreement with much of the ceramic $BaTiO_3$ data, for which $\varepsilon_r \le 1000$ at T = 500 K. This small value of A suggests that the built-in dipoles in $BaTiO_3$ are more robust than one might first think..

[1] S. Roberts, "Dielectric Constant of Barium Titanate at High Temperatures," Phys. Rev., Vol 75, p. 989 (1947).
[2] From CTE ~ 10 ppm/°C (http://www.avxcorp.com/docs/techinfo/cracks.pdf)

Review of the Coefficient of Thermal Expansion (CTE): The coefficient of thermal expansion is generally defined as the fractional increase in length per unit rise in temperature. The exact definition varies, depending on whether it is specified at a precise temperature (true coefficient of thermal expansion) or over a temperature range (mean coefficient of thermal expansion). The former is related to the slope of the tangent to the length – temperature plot, while the latter is governed by the slope of the chord between two points on this curve. Considerable variation in the value of the CTE can occur according to the definition employed.

For metallic materials values in the range 10 x 10^{-6} to 30 x 10^{-6} K^{-1} are common, and the thermal expansion of *pure metals* up to their melting points has been well characterised. However data for *engineering alloys* at very high temperatures is often limited. This is significant since there is generally a variation (usually an increase) in CTE with temperature.

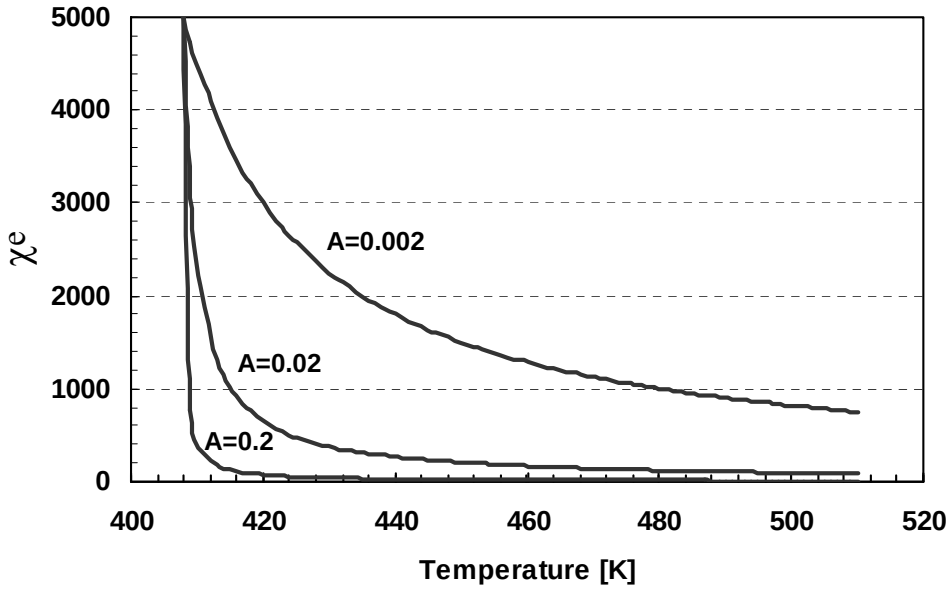

Fig. 1

Extra Problem: Polarizability of dielectric sphere

(a). We can assume the entire dielectric sphere is one dipole so that $P_e = p/V = \alpha E_0/V$ where V is the volume of the sphere. But by definition, $P_e = \varepsilon_0 \chi_e E_{in}$ where E_0 is the field outside the sphere and E_{in} is the field inside. Hence we have

$$\alpha = \varepsilon_0 \chi_e V \, E_{in}/E_0 \qquad (1)$$

The relation between E_{in} and E_o is the depolarization expression: $E_{in} = E_0 - P_e/3\varepsilon_0$, so E_{in}/E_0 is given by

$$E_{in}/E_0 = 1 - \alpha/(3\varepsilon_0 V) \qquad (2)$$

Substitution back into (1) yields

$$\alpha = V\varepsilon_0 \chi_e (1 - \alpha/3\varepsilon_0 V) \qquad (3)$$

Solving for α, we get,

$$\alpha = V\varepsilon_0 \chi_e/(1 + \chi_e/3) = V\varepsilon_0(\varepsilon_r - 1)/[1 + (\varepsilon_r - 1)/3] = 3V\varepsilon_0(\varepsilon_r - 1)/(\varepsilon_r + 2). \quad (4)$$

Substitution for the dielectric sphere volume $V = (4/3)\pi a^3$ yields the final expression

$$\alpha = 4\pi a^3 \varepsilon_0(\varepsilon_r - 1)/(\varepsilon_r + 2). \qquad (5)$$

(b) We now imagine an "effective medium" in which the dielectric spheres having polarizability given by Eqn (5) occupy space with some concentration n_s. We apply the Clausius-Mosotti relation for one dipole type to get an expression:

$$n_s\alpha/3\varepsilon_0 = (\varepsilon_{eff} - 1)/(\varepsilon_{eff} + 2) = n_s \, V \, (\varepsilon_r - 1)/(\varepsilon_r + 2) = f_r \, (\varepsilon_r - 1)/(\varepsilon_r + 2) \qquad (6)$$

where $f_r = n_s \cdot V$ is the fill fraction of the dielectric spheres in space.