

1 Maxwell-Wagner Polarization

2 Relaxation of interfacial polarization at the surface of a conducting sphere embedded in a
 3 dielectric continuum is known as *Maxwell-Wagner (MW) polarization*. Wagner [1] computed
 4 the loss tangent $\tan\delta$ for a volume fraction ϕ of spheres of material conductivity σ_1 and relative
 5 permittivity ε_1 suspended in a dielectric medium of relative permittivity ε_2 , that was then
 6 generalized by Sillars [2] to suspensions of nonspherical particles. An excellent discussion of the
 7 phenomenon is given in ref [3] from which much of the following is distilled. We also draw from
 8 the paper by van Beek [4] who gave the Sillars formula and then considered the special case of
 9 suspended spheres, and noted that the often cited Wagner formula is only correct when the
 10 permittivities of the suspended material and the dielectric medium are equal and that the Sillars
 11 expression does not have this flaw. For ellipsoids with axes a and b with the a -axis parallel to the
 12 applied electric field the Sillars expression is

$$13 \quad \tan \delta = \frac{\varepsilon_2 K}{\left[e_\infty (\varepsilon_2 K + e_\infty) \right]^{1/2}} \left(\frac{\omega \tau_0}{1 + \omega^2 \tau_0^2} \right) \quad (1)$$

14 with

$$K = \frac{n^2 \phi \varepsilon_2}{\left[(n-1) \varepsilon_2 + \varepsilon_1 \right]} \quad (a)$$

$$e_\infty = \varepsilon_2 \left[1 + \frac{n \phi (\varepsilon_2 - \varepsilon_1)}{(n-1) \varepsilon_2 + \varepsilon_1} \right] \quad (b)$$

$$15 \quad T = \frac{e_0 \left[(n-1) \varepsilon_2 + \varepsilon_1 \right]}{\sigma_1} \quad (c)$$

$$\tau_0 = \frac{T}{\left\{ (\varepsilon_1 K + e_\infty) / e_\infty \right\}^{1/2}} \quad (d)$$

16 where n is a function of the aspect ratio a/b of the suspended particles. The limiting values for n
 17 are

$$n \sim 1 \quad (a < b) \quad (a)$$

$$18 \quad n = 3 \quad (a = b) \quad (b) \quad (3)$$

$$n \approx \left\{ \frac{a^2}{b^2 \left[\ln(2a/b) - 1 \right]} \right\} \quad (a > b) \quad (c)$$

19 Equation (3)c indicates that for needle-like particles oriented in the direction of the field the
 20 value of n can be large – for example $n \sim 50$ for $a = 10b$. Because $\tan \delta$ is roughly proportional
 21 to n^2 [eqs. (1) and (2)a] the Maxwell-Wagner-Sillars effect can produce very large dielectric
 22 losses.

23 For spherical particles

$$K = \frac{9\phi\epsilon_2}{[2\epsilon_2 + \epsilon_1]}, \quad (a)$$

$$24 \quad e_\infty = \epsilon_2 \left[1 + \frac{3\phi(\epsilon_2 - \epsilon_1)}{2\epsilon_2 + \epsilon_1} \right], \quad (b) \quad (4)$$

$$T = \frac{e_0 [2\epsilon_2 + \epsilon_1]}{\sigma_1}, \quad (c)$$

25 and τ_0 is unchanged from eq. (2)a. The maximum value of $\tan \delta$ from eq. (1) is

$$26 \quad \tan \delta_{\max} = \frac{\epsilon_2 K}{2[e_\infty (\epsilon_2 K + e_\infty)]^{1/2}} \quad (5)$$

27 that is inconveniently complicated but simplifies when $\phi \rightarrow 0$:

$$28 \quad \lim_{\phi \rightarrow 0} (\tan \delta_{\max}) = \frac{9\phi\epsilon_2}{2(2\epsilon_2 + \epsilon_1)} \quad (6)$$

29 The components of the complex relative permittivity for the Maxwell-Wagner phenomenon
30 ($\phi \rightarrow 0$) are conveniently expressed using three ancillary functions [4]:

$$31 \quad \epsilon_\phi = \epsilon_2 \left\{ 1 + \frac{3\phi(\epsilon_1 - \epsilon_2)}{2\epsilon_2 + \epsilon_1} \right\}, \quad (= e_\infty ?) \quad (7)$$

$$32 \quad S = \frac{9\phi\epsilon_2}{2\epsilon_2 + \epsilon_1}, \quad (8)$$

$$33 \quad T = \frac{e_0 (2\epsilon_2 + \epsilon_1)}{\sigma_1}. \quad (9)$$

34 Then

$$35 \quad \epsilon'' = \frac{(\epsilon_\phi S \omega T)}{1 + \omega^2 T^2} \quad (10)$$

36 and

$$37 \quad \epsilon' = \epsilon_\phi \left\{ 1 + \frac{S}{1 + \omega^2 T^2} \right\}. \quad (11)$$

38 The maximum in the observed dielectric loss ϵ''_{MW} is therefore

$$39 \quad \epsilon''_{\max} = \frac{9\phi\epsilon_2^2}{2(2\epsilon_2 + \epsilon_1)} \left[1 + \frac{3\phi(\epsilon_2 - \epsilon_1)}{2\epsilon_2 + \epsilon_1} \right] \rightarrow \frac{9\phi\epsilon_2^2}{2(2\epsilon_2 + \epsilon_1)} \quad (12)$$

40 that occurs at an angular frequency ω_{\max} given by

$$41 \quad \omega_{\max} = 1/T = \frac{\sigma_1}{e_0 (2\epsilon_1 + \epsilon_2)}. \quad (13)$$

42 Supercooled Water

43 Maxwell-Wagner polarization has been used to obtain the relative permittivity of
 44 supercooled water down to about -35°C [5,6]. Before describing these results, however, two
 45 facts deserve to be mentioned: (i) The Maxwell-Wagner losses occur in the frequency range
 46 $10^5 - 10^6$ Hz that is far below the frequency range for the dielectric relaxation of water (around
 47 10^{10} Hz). Thus the measured values for the relative permittivity of water correspond to the
 48 limiting low frequency values $\varepsilon_0 \gg 80$. (ii) The relaxation frequency for ice is about $10^{3.5}$ Hz at
 49 0°C and decreases with decreasing temperature so that if crystallization occurred the relative
 50 permittivity of ice would be the limiting high frequency value $\varepsilon_{\infty} \sim 5$. It is fortunate that the
 51 Maxwell-Wagner losses occur at frequencies between the relaxation frequency ranges of water
 52 and ice.

53 Water droplets suspended in beeswax [5] and emulsions of water in heptane stabilized by
 54 the surfactant sorbitol tristearate [6] both exhibit Maxwell-Wagner polarization. In the first and
 55 rigorous beeswax study by Hasted and Shahidi [5] volume fractions of 0.5% and 1.0% were
 56 used. Later, Hodge and Angell [6] used a much larger volume fraction of water (30%) that was
 57 necessitated by their much lower instrumental sensitivity. The Hodge/Angell data were stated to
 58 be inconsistent with the Maxwell-Wagner formulae because their values of $\varepsilon''_{\text{max}}$ were claimed
 59 to be about four times larger than predicted and their sign of $(d\varepsilon''_{\text{max}}/dT) \propto (d\varepsilon_1/dT)$ was
 60 positive rather than negative as predicted by their eq. (3). However their eq. (3) is incorrect – the
 61 numerator term ε_2^2 of eq. (12) was given as ε_1^2 so that the analyses of $\varepsilon''_{\text{MW}}$ given in [6] and [8]
 62 are also incorrect. Equation (12) predicts that $\varepsilon''_{\text{max}}$ is indeed inversely proportional to ε_1 if
 63 $\varepsilon_1 \gg \varepsilon_2$ (a good approximation for water droplets in hexane). These mistakes are removed in the
 64 following discussion. The analyses in terms of the electric modulus [6,8] are unaffected and
 65 remain valid although the stated requirement that a series capacitance that simulates the
 66 surfactant layer around the droplet needs to be large for the modulus analysis to be useful [8] is
 67 not needed (see below).

68 The emulsion data differ greatly from Maxwell-Wagner predictions. Although the
 69 maxima in ε'' do indeed decrease with decreasing temperature their magnitudes are inconsistent
 70 with eq. (12): for $\varepsilon_1 \approx 100 \gg \varepsilon_2 \approx 2$ and $\phi = 0.3$ the predicted value is about
 71 $\varepsilon''_{\text{max}} \approx \{(9)(0.3)(4)/[2(106)]\} [1 - 0.9(100)/100] = (0.115)(0.1) = .0051$, compared with the
 72 experimental values that range between about 0.4 – 0.8 that are therefore too large by a factor of
 73 about 100. Also, the measured ratio of $\varepsilon''_{\text{max}}$ at the temperature extremes of 0°C and -35°C is
 74 about 1.8 compared with the correct value of about 1.2. The observed values of ω_{max} were
 75 around $2\pi(5 \times 10^5 \text{ Hz}) \approx 3 \times 10^6$ rad/s, from which eq. (13) predicts a conductivity of about
 76 $\sigma_1 \approx \varepsilon_0(2\varepsilon_1 + \varepsilon_2)\omega_{\text{max}} \approx (9 \times 10^{-12} \text{ F/m})(202)(3 \times 10^6) \approx 5 \times 10^{-3} \text{ S/m}$ that is impossibly high.

77 The modulus peak heights also decreased with decreasing temperature and since M''_{max} is
 78 assumed to be inversely proportional to the permittivity this trend is also in the correct direction.
 79 Values of ε_1 for water were then derived by assuming that $M''_{\text{max}} \propto 1/\varepsilon_1$, fixing the
 80 proportionality constant from literature data for ε_1 at 0°C , and then least squares fitting a

81 quadratic in temperature to eight data points between 0°C and –35°C. Agreement with the
 82 earlier Hasted/Shahadi results (of which the authors were unaware at the time of their paper
 83 submission) is within the ±2% uncertainties claimed for each method, but the agreement is
 84 actually better than this because most of the discrepancies are systematic due to the different
 85 values of ε_1 at 0°C for the two methods (measured in [5] but chosen from the literature to obtain
 86 the proportionality constant in [6]). When this is corrected for by equating the average of the
 87 modulus derived permittivities to the average from reference [5] the differences are reduced to
 88 0.5% or less. This is a remarkable result given the simplifications used in the modulus analysis.

89 The permittivity and modulus results for the emulsified water droplets can both be
 90 rationalized in terms of a simplified equivalent circuit: a parallel (R_1C_1) element corresponding
 91 to the water droplet with relative permittivity ε_1 and conductivity σ_1 is in series with a
 92 capacitance C_s that simulates the suspected thin layer of interfacial material, and a capacitance C_2
 93 is in parallel with the series combination to simulate the surrounding heptane. Intuitively, C_2 is
 94 much smaller than C_1 from both geometrical and physical considerations ($\varepsilon_1 \gg \varepsilon_2$). The circuit
 95 analysis is:

96 (i) Admittance A_1 of parallel (R_1C_1) element:

$$97 \quad A_1 = 1/R_1 + i\omega C_1 = (1 + i\omega R_1 C_1)/R_1 = (1 + i\omega\tau_1)/R_1 \text{ so that } Z_1 = R_1/(1 + i\omega\tau_1).$$

$$98 \quad \text{(ii) Impedance of } \{(R_1C_1) + C_s\} \text{ arm} = Z_{1s} = \frac{R_1}{1 + i\omega\tau_1} + \frac{1}{i\omega C_s} = \frac{i\omega R_1 C_s + 1 + i\omega\tau_1}{i\omega C_s(1 + i\omega\tau_1)}$$

$$99 \quad \Rightarrow A_{1s} = \frac{i\omega C_s(1 + i\omega\tau_1)}{1 + i\omega(\tau_1 + R_1 C_s)}.$$

100 (iii) Admittance A_{1s2} of complete circuit:

$$101 \quad A_{1s2} = A_{1s} + i\omega C_2 = \frac{i\omega C_s - \omega^2 C_s \tau_1 + i\omega C_2 [1 + i\omega(\tau_1 + R_1 C_s)]}{1 + i\omega(\tau_1 + R_1 C_s)}$$

$$102 \quad = \frac{i\omega(C_s + C_2) - \omega^2(C_s \tau_1 + C_2 \tau_1 - R_1 C_s C_2)}{1 + i\omega(\tau_1 + R_1 C_s)}.$$

103 (iv) For $C_2 \ll C_1, C_s$ appropriate for water droplets in heptane the admittance simplifies to

$$104 \quad A_{1s2} = \frac{i\omega C_s - \omega^2 R_1 C_1 C_s}{1 + i\omega R_1 (C_1 + C_s)}$$

105 and

$$106 \quad C_{1s2}^* = \frac{A_{1s2}}{i\omega} = \frac{C_s(1 + i\omega R_1 C_1)}{1 + i\omega R_1 C_s} = \frac{C_s(1 + i\omega R_1 C_1)(1 + i\omega R_1 C_s)}{1 + \omega^2 R_1^2 C_s^2}$$

$$= \frac{C_s - \omega^2 R_1^2 C_1 C_s}{1 + \omega^2 R_1^2 C_s^2} + \frac{i\omega R_1 C_s (C_1 + C_s)}{1 + \omega^2 R_1^2 C_s^2}. \quad (14)$$

107 Thus the maximum value of C'' is $(C_1 + C_s)/2$ and is therefore determined in part by the
 108 surfactant layer and is greater than the value $C_1/2$ for no series capacitance. This is consistent
 109 with the observed maxima in ε'' [6] being about 100 times greater than that calculated from the

110 Maxwell-Wagner expression if $C_s \approx 100C_1$. The maximum in C'' occurs at $\omega_{\max} = 1/(R_1C_s)$ that
 111 is also determined in part by the surfactant layer. This dependency of the relaxation time on C_s
 112 can account for the (unreported) fact that changing the suspending medium changed ω_{\max} , since
 113 the suspending medium would be expected to affect the surfactant layer and C_s .

114 The imaginary component of the electric modulus for $C_2 \ll C_1$ is

$$115 \quad M'' = \frac{i\omega R_1}{(1+i\omega^2 R_1^2 C_1^2)} = \left(\frac{1}{C_1}\right) \frac{i\omega R_1 C_1}{(1+i\omega^2 R_1^2 C_1^2)}, \quad (15)$$

116 the maximum value of which is $1/(2C_1)$ and contains the desired information about C_1 that is
 117 independent of C_s . The frequency of maximum M'' is $\omega_{\max} = 1/(R_1C_1)$ and is also independent of
 118 C_s . These results obtain because C_2 is much smaller than C_1 and do not depend on C_s being much
 119 larger than C_1 , as stated earlier [6,8].

120 GNU Octave calculation of the relaxation functions for the circuit enables values of the
 121 circuit elements to be estimated that produce trends that are generally consistent with the
 122 experimental data. Good agreement with the experimental trends is attained with $R_1 = 10^3$;
 123 $C_1 = 10^{-3}$; $C_2 = 10^{-5}$; $C_s = 5 \times 10^{-4}$. The value of 100 for the ratio C_1/C_2 was chosen to be about
 124 twice the ratio of permittivities of water and hexane and to accommodate an unknown geometric
 125 factor for the suspending medium relative to the droplet, and the value of C_s was found from the
 126 experimental ratio of 0.5 for the frequencies of maximum ε'' and M'' (the latter being higher).
 127 The geometric factor is probably the largest source of uncertainty in the circuit parameters.

128 Equation (14) indicates that the maximum value of ε'' should be increased by a factor of
 129 $(C_1 + C_s)/C_1 \approx 100$ over that for no surfactant, consistent with the experimental factor of about
 130 100 noted above.

131 The Maxwell-Wagner equivalent circuit discussed here is clearly crude but serves to
 132 rationalize the remarkable success of the electric modulus in analyzing the Maxwell-Wagner
 133 effect for water droplets in a dielectric medium of low permittivity.

134

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