

## 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 the  
 4 loss tangent  $\tan \delta$  for a volume fraction  $\phi$  of spheres of material with conductivity  $\sigma_1$  and relative  
 5 permittivity  $\varepsilon_1$  suspended in a dielectric medium of relative permittivity  $\varepsilon_2$ , 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. The relative  
 8 permittivity for Maxwell-Wagner polarization of dispersed spherical conducting particles is [3]

$$9 \quad \varepsilon' = \varepsilon_\phi \left[ 1 + \frac{3\phi(\varepsilon_1 - \varepsilon_2)}{2\varepsilon_2 + \varepsilon_1} \right], \quad (1)$$

10 where

$$11 \quad \varepsilon_\phi = \varepsilon_2 \left\{ 1 + \frac{3\phi(\varepsilon_1 - \varepsilon_2)}{2\varepsilon_2 + \varepsilon_1} \right\}. \quad (2)$$

12 The dielectric loss is

$$13 \quad \varepsilon'' = \frac{\varepsilon_\phi S \omega T}{1 + \omega^2 T^2}, \quad (3)$$

14 where

$$15 \quad S = \frac{9\phi\varepsilon_2}{2\varepsilon_2 + \varepsilon_1}, \quad (4)$$

$$16 \quad T = \frac{\varepsilon_0(2\varepsilon_2 + \varepsilon_1)}{\sigma_1}. \quad (5)$$

17 The maximum value of the observed dielectric loss from eq. (3) is

$$18 \quad \varepsilon''_{\max} = \frac{9\phi\varepsilon_2^2}{2(2\varepsilon_2 + \varepsilon_1)} \left[ 1 + \frac{3\phi(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_2 + \varepsilon_1} \right] \quad (6)$$

19 that in the limit  $\phi \rightarrow 0$  is

$$20 \quad \varepsilon''_{\max} = \frac{9\phi\varepsilon_2^2}{2(2\varepsilon_2 + \varepsilon_1)}. \quad (7)$$

21 This maximum occurs at an angular frequency  $\omega_{\max}$  given by

$$22 \quad \omega_{\max} = 1/T = \frac{\sigma_1}{\varepsilon_0(2\varepsilon_2 + \varepsilon_1)}, \quad (8)$$

23 independent of  $\phi$ . For the case of supercooled water discussed below  $\varepsilon_1 \gg \varepsilon_2$  and eq. (6)  
 24 simplifies to

$$25 \quad \varepsilon''_{\max} = \frac{9\phi\varepsilon_2^2}{2\varepsilon_1} [1 - 3\phi]. \quad (9)$$

26

## 27 Supercooled Water

28 Maxwell-Wagner polarization has been used to obtain the relative permittivity of  
 29 supercooled water down to about  $-35^{\circ}\text{C}$  [4,5]. Before describing these results, however, two facts  
 30 deserve to be mentioned. (i) The Maxwell-Wagner losses occur in the frequency range  $10^5 - 10^6$   
 31 Hz that is far below the frequency range for the dielectric relaxation of water (around  $10^{10}$  Hz).  
 32 Thus the measured values for the relative permittivity of water correspond to the desired limiting  
 33 low frequency values, around 80. (ii) The relaxation frequency for ice is about  $10^{3.5}$  Hz at  $0^{\circ}\text{C}$  and  
 34 decreases with decreasing temperature, so that if crystallization occurred the appropriate relative  
 35 permittivity of ice for the MW effect would be its limiting high frequency value, around 5. It is  
 36 fortunate that the Maxwell-Wagner losses occur at frequencies between the relaxation frequency  
 37 ranges of water and ice.

38 Water droplets suspended in beeswax [4] and emulsions of water in heptane stabilized by  
 39 the surfactant sorbitol tristearate [5] both exhibit Maxwell-Wagner polarization. In the first and  
 40 rigorous beeswax study by Hasted and Shahidi [4] volume fractions of 0.005 and 0.01 were used  
 41 and eq. (7) is appropriate. Later, Hodge and Angell [5] used a much larger volume fraction of  
 42 water (0.3) that was necessitated by their much lower instrumental sensitivity and in this case eq.  
 43 (6) is presumably better (but see below). The Hodge/Angell data were stated to be inconsistent  
 44 with the Maxwell-Wagner formulae in part because their observed sign of  
 45  $(d\varepsilon''_{\text{max}}/dT) \propto (d\varepsilon_1/dT)$  was negative rather than positive as predicted by their eq. (3). However  
 46 their eq. (3) is incorrect because the numerator term  $\varepsilon_2^2$  of eq. (7) was given as  $\varepsilon_1^2$ . This mistake  
 47 is corrected in the following discussion – both eqs. (6) and (7) predict that  $\varepsilon''_{\text{max}}$  is indeed inversely  
 48 proportional to  $\varepsilon_1$  if  $\varepsilon_1 \gg \varepsilon_2$  (a good approximation for water droplets in hexane). However, the  
 49 second term in eq. (6) becomes negative for  $\phi > 1/3$  and  $\varepsilon_1 \gg \varepsilon_2$  (eq. (9)), suggesting that the  
 50 MW analysis probably breaks down for the Hodge/Angell data in any case. The analysis in terms  
 51 of the electric modulus given in [5] is however unaffected and remains valid, although the  
 52 statement there that the series capacitance that simulates the surfactant layer around the droplet  
 53 needs to be large for the modulus analysis to be useful is incorrect.

54 In keeping with the caveats stated above the emulsion data reported in [5] differed from  
 55 Maxwell-Wagner predictions. Although the maxima in  $\varepsilon''$  did indeed decrease with decreasing  
 56 temperature their magnitudes were inconsistent with eq. (7): for  $\varepsilon_1 \approx 100 \gg \varepsilon_2 \approx 2$  and  $\phi = 0.3$  the  
 57 predicted value is about  $\varepsilon''_{\text{max}} \approx [(9)(0.3)(4)/200](0.1) \approx 0.0054$ , compared with the  
 58 experimental values that range between about 0.4 – 0.8 that are therefore too large by a factor of  
 59 about 100. Even if eq. (7) was used instead of eq. (6) the factor would be 10 and the problem would  
 60 remain. The observed values of  $\omega_{\text{max}}$  were around  $2\pi(5 \times 10^5 \text{ Hz}) \approx 3 \times 10^6$  rad/s, from which eq.  
 61 (8) predicts a conductivity of about  $\sigma_1 \approx (9 \times 10^{-12} \text{ F/m})(104)(3 \times 10^6) \approx 3 \times 10^{-3}$  S/m that, as noted  
 62 in [5], is about that of a  $3 \times 10^{-4}$  molar solution of NaCl.

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

67 in temperature to eight data points between 0°C and -35°C. Agreement with the earlier  
 68 Hasted/Shahadi results (of which the authors were unaware at the time of submission) is within  
 69 the  $\pm 2\%$  uncertainties claimed for each method, but the agreement is actually better than this  
 70 because most of the discrepancies are systematic due to the different values of  $\varepsilon_1$  at 0°C for the  
 71 two methods (measured in [4] but chosen from the literature to obtain the proportionality constant  
 72 in [5]). When this is corrected for by equating the average of the modulus derived permittivities to  
 73 the average from reference [4] the differences are reduced to 0.5% or less [6]. This is a remarkable  
 74 result given the simplifications used in the modulus analysis.

75 The permittivity and modulus results for the emulsified water droplets can both be  
 76 rationalized in terms of a simplistic equivalent circuit: a parallel ( $R_1C_1$ ) element corresponding to  
 77 the water droplet with relative permittivity  $\varepsilon_1$  and conductivity  $\sigma_1$  is in series with a capacitance  
 78  $C_s$  that simulates the suspected thin layer of interfacial material, and a capacitance  $C_2$  is in parallel  
 79 with the series combination to simulate the surrounding heptane. The value of  $C_1$  is much greater  
 80 than  $C_2$  since  $\varepsilon_1 \gg \varepsilon_2$ . The circuit analysis is:

81 (i) Admittance  $A_1$  of parallel ( $R_1C_1$ ) element:

82 
$$A_1 = 1/R_1 + i\omega C_1 = (1 + i\omega R_1 C_1)/R_1 = (1 + i\omega\tau_1)/R_1$$
 so that  $Z_1 = R_1/(1 + i\omega\tau_1)$ .

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

84 
$$\Rightarrow A_{1s} = \frac{i\omega C_s(1 + i\omega\tau_1)}{1 + i\omega(\tau_1 + R_1 C_s)}$$

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

86 
$$A_{1s2} = A_{1s} + i\omega C_2 = \frac{i\omega C_s - \omega^2 C_s \tau_1 + i\omega C_2 [1 + i\omega(\tau_1 + R_1 C_s)]}{1 + i\omega(\tau_1 + R_1 C_s)}$$

87 
$$= \frac{i\omega(C_s + C_2) - \omega^2(C_s \tau_1 + C_2 \tau_1 - R_1 C_s C_2)}{1 + i\omega(\tau_1 + R_1 C_s)}$$

88 (iv) For  $C_1 \gg C_2$  appropriate for water droplets in heptane the admittance simplifies to

89 
$$A_{1s2} = \frac{i\omega C_s - \omega^2 R_1 C_1 C_s}{1 + i\omega R_1 (C_1 + C_s)}$$

90 and the complex capacitance is

91 
$$C_{1s2}^* = \frac{A_{1s2}}{i\omega} = \frac{C_s(1 + i\omega R_1 C_1)}{1 + i\omega R_1 C_s} = \frac{C_s(1 + i\omega R_1 C_1)(1 + i\omega R_1 C_s)}{1 + \omega^2 R_1^2 C_s^2}$$
 (10)

92 
$$= \frac{C_s - \omega^2 R_1^2 C_1 C_s}{1 + \omega^2 R_1^2 C_s^2} + \frac{i\omega R_1 C_s (C_1 + C_s)}{1 + \omega^2 R_1^2 C_s^2}$$

92 The maximum value of  $C''$  is  $(C_1 + C_s)/2$  and is therefore determined in part by the surfactant  
 93 layer. This is consistent with the observed maxima in  $\varepsilon''$  being about 100 times greater than that  
 94 calculated from the Maxwell-Wagner expression if  $C_s = 99C_1$ , a sensible value.

95 The predicted maximum in  $C''$  occurs at  $\omega_{\max} = 1/(R_1 C_s)$  that is also determined in part by

96 the surfactant layer. This dependency of the relaxation time on  $C_s$  can account for the (unreported)  
 97 fact that changing the suspending medium changed  $\omega_{\max}$ , since the suspending medium would be  
 98 expected to affect the surfactant layer and  $C_s$ . This dependency could also account for the  
 99 suspiciously high value of the conductivity of the water droplets.

100 The imaginary component of the electric modulus for  $C_1 \gg C_2$  is

$$101 \quad M'' = \frac{i\omega R_1}{(1+i\omega^2 R_1^2 C_1^2)} = \left(\frac{1}{C_1}\right) \frac{i\omega R_1 C_1}{(1+i\omega^2 R_1^2 C_1^2)}, \quad (11)$$

102 the maximum value of which is  $1/(2C_1)$  and contains the desired information about  $C_1$  that is  
 103 independent of  $C_s$ . The frequency of maximum  $M''$  is  $\omega_{\max} = 1/(R_1 C_1)$  and is also independent of  
 104  $C_s$ . These results obtain because  $C_1$  is much greater than  $C_2$  and do not depend on  $C_s$  being much  
 105 larger than  $C_1$ , as stated earlier [5,6].

106 GNU Octave calculation of the relaxation functions for the circuit enables values of the  
 107 circuit elements to be estimated that reproduce trends that are consistent with the experimental  
 108 data. Good agreement with experiment is attained with  $R_1 = 10^3$ ;  $C_1 = 10^{-3}$ ;  $C_2 = 10^{-5}$ . The value  
 109 of 100 for the ratio  $C_1/C_2$  is about twice the ratio of permittivities of water and hexane and was  
 110 chosen in part to accommodate unknown geometric factors. These geometric factors are  
 111 undoubtedly the largest source of uncertainty in the circuit parameters.

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

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## 117 REFERENCES

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