

CHAPTER TWO ELECTRICAL RELAXATION
[NO FIGURE VERSION]

1
2
3
4 **3/4/2017 4:09 AM**

5 Contents

6	PRELIMINARIES	3
7	2.1 NOMENCLATURE	3
8	2.2 ELECTROMAGNETISM	3
9	2.2.1 UNITS	3
10	2.2.2 ELECTROMAGNETIC QUANTITIES	5
11	2.2.3 ELECTROSTATICS	7
12	2.2.3.1 <i>Point Charge (Coulomb's Law)</i>	7
13	2.2.3.2 <i>Long Thin Rod with Uniform Linear Charge Density λ</i>	7
14	2.2.3.3 <i>Large Flat Insulating Plate</i>	8
15	2.2.3.4 <i>Large Flat Conducting Plate</i>	8
16	2.2.3.5 <i>Two Large Parallel Insulating Flat Plates</i>	8
17	2.2.3.6 <i>Two Large Parallel Conducting Flat Plates</i>	8
18	2.2.3.7 <i>Concentric Conducting Cylinders</i>	9
19	2.2.3.8 <i>Concentric Conducting Spheres</i>	9
20	2.2.3.9 <i>Isolated Sphere</i>	10
21	2.2.4 ELECTRODYNAMICS	10
22	2.2.5 MAXWELL'S EQUATIONS	11
23	2.2.6 ELECTROMAGNETIC WAVES	13
24	2.2.7 LOCAL ELECTRIC FIELDS	16
25	2.2.8 CIRCUITS	17
26	2.2.8.1 <i>Simple Circuits</i>	17
27	2.2.8.2 <i>AC Circuits</i>	19
28	2.2.8.3 <i>Experimental Factors</i>	23
29	2.3 DIELECTRIC RELAXATION	25
30	2.3.1 FREQUENCY DOMAIN	25
31	2.3.1.1 <i>Dipole Rotation</i>	25
32	2.3.1.2 <i>Ionic Hopping</i>	30
33	2.3.2 TIME DOMAIN	30
34	2.3.3 TEMPERATURE DOMAIN	31
35	2.3.4 EQUIVALENT CIRCUITS	33
36	2.3.5 INTERFACIAL POLARIZATION	34
37	2.3.6 MAXWELL-WAGNER POLARIZATION	35
38	2.3.7 EXAMPLES	37
39	2.3.7.1 <i>Liquid Water</i>	37
40	2.3.7.2 <i>Supercooled Water</i>	38
41	2.3.7.3 <i>Hydration Water</i>	41
42	2.4 CONDUCTIVITY RELAXATION	43
43	2.4.1 GENERAL ASPECTS	43

44	2.4.2	DISTRIBUTION OF CONDUCTIVITY RELAXATION TIMES.....	45
45	2.4.3	CONSTANT PHASE ELEMENT ANALYSIS	46
46	2.4.4	DETERMINATION OF σ_0	48
47	2.4.4.1	<i>Analyses in the Complex Resistivity Plane.....</i>	48
48	2.4.4.2	<i>Modulus and Resistivity Spectra</i>	48
49	2.4.4.3	<i>Complex Admittance Plane.....</i>	49
50	2.4.5	COMBINED CONDUCTIVITY AND DIELECTRIC RELAXATION	49
51	2.4.6	EXAMPLES.....	50
52	2.4.6.1	<i>Electrode Polarization and Bulk Relaxation in the Frequency Domain</i>	50
53	2.4.6.2	<i>Conductivity Relaxation in Sodium β – Alumina</i>	51
54	2.4.6.3	<i>Complex Impedance Plane Analysis of Electrode Polarization in Sintered β – Alumina.</i>	52
55	2.4.6.5	<i>Intergranular Effects in Polycrystalline Electrolytes</i>	53
56	2.4.6.6	<i>Intergranular Cracking</i>	53
57	2.4.6.7	<i>Intergranular Gas Adsorption</i>	54
58	APPENDIX 2.1 – DERIVATION OF M^* FOR A DEBYE RELAXATION WITH NO		
59	ADDITIONAL SEPARATE CONDUCTIVITY		56
60	COMPUTATION CODE FOR A DEBYE RELAXATION WITH ADDITIONAL SEPARATE		
61	CONDUCTIVITY σ_0		58
62	APPENDIX 2.3 DERIVATION OF DEBYE DIELECTRIC EXPRESSION FROM		
63	EQUIVALENT CIRCUIT.....		59
64			
65			

66 Preliminaries (include in Book Prologue)

67 The examples used to illustrate different applications are not central to the purpose of this
68 book and are not recent. Some of the applications have been discussed in an unpublished but
69 widely circulated paper by the present author that is available at
70 [http://imhodge.startlogic.com/pdfs/ac%20data%20analysis\(final\).pdf](http://imhodge.startlogic.com/pdfs/ac%20data%20analysis(final).pdf).

71
72 2.1 Nomenclature

73 Italicized lower case letters are used for physical variables, e.g. $\{x, y, z, r\}$ for distances, t
74 for time, and q for charge; italicized upper case letters are used for specific values of variables
75 and field magnitudes, e.g. $\{X, Y, Z, R\}$, T, Q . Vectors are denoted by bold face upper case letters
76 with an arrow \vec{V} and tensors are denoted by bold face upper case \mathbf{T} .

77 There are two time constants for relaxation of polarization, one for relaxation at constant
78 electric field (i.e. dielectric relaxation of the displacement \vec{D}) denoted by τ_E and one for
79 relaxation at constant displacement (i.e. conductivity relaxation of the electric field \vec{E}) denoted
80 by τ_D . Amongst other things these two distinct time constants correspond to two microscopic
81 time constants for a single macroscopic dielectric time constant, as has been briefly discussed in
82 ref. [1].

83 Dielectric and conductivity relaxations can both occur in the same material over two
84 resolvable frequency ranges and the usual nomenclature for the low and high frequency limits of
85 a single relaxation process (e.g. ϵ_0 and ϵ_∞ for the relative permittivity) is ambiguous and has
86 caused confusion in a long-standing debate about the legitimacy of the electric modulus
87 formalism. We introduce a new nomenclature here to distinguish the low and high frequency
88 limits for the two possible relaxations that, although somewhat clumsy, eliminates this
89 confusion. The two limits for a dielectric relaxation at constant \vec{E} are denoted by ϵ_0^E and ϵ_∞^E and
90 the two limits for a conductivity relaxation at constant \vec{D} are denoted by ϵ_0^D and ϵ_∞^D . Since a
91 conductivity relaxation must occur at lower frequencies than a dielectric relaxation for the latter
92 to be readily observed (with some exceptions depending on instrumental sensitivity) then
93 $\epsilon_\infty^D = \epsilon_0^E$.

94 Electric charge is denoted by q (Coulomb C), volume charge density by ρ (C m^{-3}),
95 surface charge density by σ C m^{-2} , linear charge density by λ C m^{-1} , current by I (Ampere = A =
96 C s^{-1}), current density by J (A m^{-2}), electric potential by ϕ_E ($\text{V}=\text{JC}^{-1}$), electric field by E
97 ($\text{NC}^{-1} = \text{V m}^{-1}$), electric dipole moment by μ_E (C.m), resistance by R (Ohm = $\Omega = \text{VA}^{-1}$), and
98 capacitance by C (Farad $\text{F} = \text{CV}^{-1}$). The SI unit for conductance (=1/resistance) is the Siemen S
99 (equal to Ω^{-1}).

100
101 2.2 Electromagnetism

102 2.2.1 Units

103 Two systems of electromagnetic units are in use, the cgs (centimeter-gram-second) and
104 the MKS (meter-kilogram-second) or SI (Systeme Internationale). The SI system is the official

105 scientific system but the cgs system appears in older publications and since it is still used by
 106 chemists and materials scientists its relationship to the SI system is delineated here. For
 107 mechanics only the numerical value of physical quantities changes with the system of units, but
 108 in electromagnetism there is an additional difference of approach: electric charge in the cgs
 109 system is defined in units of mass-length-time whereas in the SI it is defined to be just as
 110 fundamental as mass, length and time: this SI unit of charge is the Coulomb. Other similar
 111 non-electromagnetic differences occur: for example the SI temperature unit K (Kelvin) is also
 112 considered to be a fundamental unit.

113 The cgs form of Coulomb's law for the force F between two point charges q_1 and q_2
 114 separated by a distance r and immersed in a medium of permittivity ϵ is
 115

$$116 \quad F = \frac{q_1 q_2}{\epsilon r^2}, \quad (2.1)$$

117
 118 that gives dimensions of $M^{1/2}L^{3/2}T^{-1}$ for the *electrostatic unit* (esu) of charge. The cgs equation
 119 for the magnetic force between two straight parallel conductors of length L carrying currents I_1
 120 and I_2 and separated by a distance r in a material of magnetic permeability μ is
 121

$$122 \quad F = \frac{2\mu L I_1 I_2}{r}, \quad (2.2)$$

123
 124 that gives dimensions of $M^{1/2}L^{1/2}$ for the *electromagnetic unit* (emu) of charge. The esu and emu
 125 units differ by a factor LT^{-1} that has the dimensions of speed and the value of the speed of light,
 126 c . This is the reason that c enters into many cgs formulae. Numerically, $\text{emu} = c \text{esu}$ (c in cgs
 127 units = 2.9979×10^{10} cm/s).

128 The Coulomb C is defined experimentally by its time derivative, the current in *amperes*
 129 A, that in turn is determined using eq. (2.2). A constant μ_0 is inserted into the SI form for this
 130 magnetic force to ensure that the same force is produced by the same currents separated by the
 131 same distance:
 132

$$133 \quad F = \frac{\mu\mu_0 L I_1 I_2}{4\pi r}. \quad (2.3)$$

134
 135 Equations (2.2) and (2.3) reveal that $\mu_0 = 4\pi \times 10^{-7} \text{ N}\cdot\text{A}^{-2}$. The factor 4π arises from *Gauss's*
 136 *Law* (eq. (1.150) and eq. (2.18) below). The SI form of Coulomb's law is
 137

$$138 \quad F = \frac{q_1 q_2}{4\pi \epsilon_0 \epsilon r^2}, \quad (2.4)$$

139
 140 where ϵ_0 is a constant (the *permittivity* of free space) with dimensions $Q^2 M^{-1} L^{-3} T^2$ that
 141 correspond to the units of capacitance per unit length (Farads meter⁻¹). Its numerical value is

142 $8.854187818 \times 10^{-12}$ Farad m^{-1} . The numerical relations between C, esu and emu are
 143 $C \approx 3 \times 10^9 \text{esu} \approx 10^{-1} \text{emu}$, where the approximate equality arises from placing the speed of
 144 light at 3×10^8 m/s rather than $2.9979... \times 10^8$ m/s. The dimensionless fine structure constant α
 145 in cgs units is $\alpha = e^2 / \hbar c = 2\pi e^2 / \hbar c$ and in SI units is $\alpha = 2\pi e^2 / 4\pi e_0 \hbar c = e^2 / 2e_0 \hbar c$. It is
 146 readily confirmed that this SI value of α is dimensionless and has the same numerical value as
 147 the cgs value. The quantity $(e_0 \mu_0)^{-1/2}$ equals the speed of light so that e_0 is
 148 $e_0 = 1 / c^2 \mu_0 = 1 / (2.9979... \times 10^8)^2 (4\pi \times 10^{-7})$.

149 The cgs system having been illustrated to this point is now dispensed with and only the SI
 150 system is used from here on apart from some tabulated expressions and one occasional exception
 151 - the unit for the molecular dipole moment. In the SI system this is the coulomb-meter but this
 152 unit is inconveniently large and is rarely used. The more common unit is the *Debye*, defined as
 153 the dipole moment created by two opposite charges of 10^{-10} esu (3.3×10^{-20} C) separated by 1.0
 154 Angstrom (10^{-10} m). The persistence of this unit probably originates in the facts that (a)
 155 molecular dipole moments are of order unity when expressed in Debyes but of order 10^{-30} in
 156 coulomb-meters; (b) chemists and materials scientists still insist on using the Debye. It is not
 157 clear to this author why a convenient SI unit such as 10^{-31} C.m ≈ 0.33 Debye or 10^{-30} C.m
 158 ≈ 3.3 Debye has not been introduced, especially since the SI unit nm has rapidly replaced the
 159 Angstrom in optical spectroscopy.

160

161 2.2.2 Electromagnetic Quantities

162 Many of these are conveniently defined using a parallel plate capacitor comprising two
 163 conducting flat plates, each of area A and separated by a distance d . The geometric "cell
 164 constant" k is

$$165 \quad k \equiv d / A. \quad (2.5)$$

166 Each plate has a charge of magnitude q_0 but of opposite sign (uniformly distributed since the
 167 plates are conducting) that produces a potential difference V between the plates. The
 168 capacitance is $C \equiv q_0 / V$ with unit Farad = C V^{-1} . The surface charge density $\sigma_0 = \pm q_0 / A$ on
 169 the plates induces an interfacial charge density $\mp \sigma_i$ on each surface of any dielectric material
 170 between the plates. The *electric field* \vec{E} , *polarization* \vec{P} and *displacement vector* \vec{D} are
 171 orthogonal to the plates with magnitudes defined by the following table:

172

SI	cgs	
$D = \sigma_0$	$D = 4\pi \sigma_0$	(2.6)
$P = \sigma_i$	$P = \sigma_i$	(2.7)
$e_0 E = \sigma_0 - \sigma_i = D - P$	$E = 4\pi(\sigma_0 - \sigma_i) = D - 4\pi P$	(2.8)

177

178 The charge densities σ_0 and σ_i generate an electrostatic potential ϕ_E (in volts) and net volume
 179 charge density ρ for which

180

$$181 \quad \vec{\mathbf{D}} = \nabla \rho \quad (2.9)$$

182 and

$$183 \quad \vec{\mathbf{E}} = \nabla \varphi_E. \quad (2.10)$$

184

185 The inverse of eq. (2.10) is

186

$$187 \quad \varphi_{1,2} = \int_{s_1}^{s_2} \vec{\mathbf{E}} \cdot d\vec{\mathbf{s}} \quad (2.11)$$

188

189 where $\vec{\mathbf{s}}$ is the displacement vector in the direction of $\vec{\mathbf{E}}$ and $\varphi_{1,2}$ is the potential difference

190 between the points s_1 and s_2 . The *relative permittivity* ε and *dielectric susceptibility* χ_d are

191 defined in the following table:

192

SI	cgs	
$\varepsilon \equiv \frac{D}{e_0 E}$	$\varepsilon \equiv \frac{D}{E}$	(2.12)

$\chi_d = \frac{P}{e_0 E} = \frac{D - e_0 E}{e_0 E} = \varepsilon - 1$	$\chi_d = \frac{P}{E} = \frac{D - E}{4\pi E} = \frac{1}{4\pi}(\varepsilon - 1)$	(2.13)
------------------------------------------------------------------------	---------------------------------------------------------------------------------	--------

196 A dielectric material between the plates decreases the electric field between the plates

197 because the induced polarization charge density σ_i on the surface of the material partly cancels

198 the unchanged charge density on the plates [eq. (2.8)]. The units of D and P (charge area⁻¹)

199 correspond to dipole moment (charge-distance) per unit volume. In view of $\vec{\mathbf{D}}$, $\vec{\mathbf{E}}$ and $\vec{\mathbf{P}}$ being

200 vectors the relative permittivity and dielectric susceptibility are in general tensors but for

201 isotropic media (liquids, glasses, and isotropic crystals) D , E , P and ε are all scalars. We mostly

202 treat them as scalars in this book.

203 The magnetic analogs of D , E , P , e_0 , ε and χ_d are, respectively, the magnetic induction

204 B , the magnetic field H , the magnetization M , the permeability of free space, μ_0 , the relative

205 permeability μ , and the magnetic susceptibility χ_m . The SI and cgs definitions are

206

SI	cgs	
$B = \mu_0 H$	$B = H$	(2.14)

$M = \frac{B}{\mu_0} - H$	$M = \frac{B - H}{4\pi}$	(2.15)
---------------------------	--------------------------	--------

$\mu = \frac{B}{H}$	$\mu = \frac{B}{H}$	(2.16)
---------------------	---------------------	--------

$\chi_M = \frac{M}{H} = \frac{B}{\mu_0 H} - 1$	$\chi_M = \frac{M}{H} = \frac{B}{4\pi H} - 1$	(2.17)
------------------------------------------------	-----------------------------------------------	--------

212
 213 2.2.3 Electrostatics
 214 Gauss's Law is
 215

$$216 \oint_S \epsilon_0 \epsilon \vec{E} \cdot d\vec{A} = q_{\text{enclosed}} \Rightarrow \oint_S \vec{D} \cdot d\vec{A} = q_{\text{free}} \quad (2.18)$$

217
 218 where q_{enclosed} is the total net charge within a closed surface of magnitude A , ϵ is the relative
 219 permittivity¹ of the material enclosed by the surface, and the surface integral is the flux of the
 220 electric field through the surface. For the definition in terms of \vec{D} the quantity q_{free} does *not*
 221 include the induced polarization charges because these are subsumed into the permittivity $\epsilon_0 \epsilon$.
 222 Equation (2.18) is the electrical version of the mathematical Gauss's Theorem in Chapter One
 223 [eq. 1.146]. As noted in Chapter One the differential area vector $d\vec{A}$ of a surface is defined as
 224 having a direction perpendicular to the plane of the surface, and for closed surfaces such as occur
 225 in Gauss's Law the outward pointing direction is defined to be positive. The Gaussian surface is
 226 a purely mathematical object that can be placed anywhere although it must have the same
 227 symmetry as the system under study to be helpful. Thus information about charge distribution
 228 can be inferred even though E is determined by the *total* enclosed charge.

229 We now apply Gauss's Law to calculate \vec{E} and the capacitance C for several electrical
 230 geometries and charge distributions. The geometrical objects and charges are taken to be
 231 immersed in a medium of relative permittivity ϵ .
 232

233 2.2.3.1 Point Charge (Coulomb's Law)

234 Define the Gaussian surface S as a sphere of radius r with a point charge q at its center.
 235 By symmetry \vec{E} is everywhere parallel to $d\vec{a}$ and has a constant magnitude E obtained from
 236 $\epsilon_0 \epsilon \oint \vec{E} \cdot d\vec{A} = 4\pi r^2 \epsilon_0 \epsilon E$ so that

$$238 E = \frac{q}{4\pi \epsilon \epsilon_0 r^2}. \quad (2.19)$$

240 2.2.3.2 Long Thin Rod with Uniform Linear Charge Density λ

241 Let the Gaussian surface be a cylinder of radius r and length L , with the rod as its
 242 coaxial central axis. Then $\epsilon \epsilon_0 \oint_S \vec{E} \cdot d\vec{A} = \epsilon \epsilon_0 E (2\pi r L) = q = \lambda L$ so that at a distance r from the

243 axis
 244

¹ Too often called the "dielectric constant" which is misleading because it is not constant (it varies with temperature and frequency for example).

$$E = \frac{\lambda}{2\pi\epsilon\epsilon_0 r}. \quad (2.20)$$

246

247 2.2.3.3 Large Flat Insulating Plate

248 Let a charge q be uniformly distributed over the two sides of an infinite², flat insulating
 249 plate of area A so that the charge on each surface is $q/2$. Define σ as the charge per unit area so
 250 that the charge density on each surface is $\sigma/2$. Define the Gaussian surface as a cylinder whose
 251 axis is parallel with the area vector of one plate and has one end inside the plate and the other
 252 end in a medium of relative permittivity ϵ . Then the electric field points away from each surface
 253 of the plate (since q is positive) and $\epsilon\epsilon_0 \oint_S \vec{E} \cdot d\vec{A} = \epsilon\epsilon_0 E(A) = q/2 = \sigma A/2$ so that

254

$$E = \frac{\sigma}{2\epsilon_0\epsilon}. \quad (2.21)$$

256

257 The electric field is therefore independent of distance from the plate.

258

259 2.2.3.4 Large Flat Conducting Plate

260 Let the charge on each side of the plate be $q/2$ and define the Gaussian surface to be the
 261 same as that for the insulating plate in §2.2.3.3. The electrostatic field inside a conductor is zero
 262 so that the electric field points away each surface of the plate and
 263 $\epsilon_0\epsilon \oint_S \vec{E} \cdot d\vec{A} = \epsilon_0\epsilon E(A) = q/2 = \sigma A/2$ so that

264

$$E = \frac{\sigma}{2\epsilon\epsilon_0}. \quad (2.22)$$

266

267 This electric field again does not depend on distance from the plate.

268

269 2.2.3.5 Two Large Parallel Insulating Flat Plates

270 Consider charges $\pm q$ that are uniformly distributed over the two surfaces of each plate.
 271 The field between the plates is the vector sum of the fields from each plate. Since the field from
 272 the positively charged plate points away from the positive plate and the field from the negatively
 273 charged plate points toward the negative plate the two fields add up as vectors to

274

$$E = \frac{\sigma}{\epsilon\epsilon_0}. \quad (2.23)$$

276

277 2.2.3.6 Two Large Parallel Conducting Flat Plates

278 The charges $\pm q$ on each plate are attracted to the opposite charges on the other plate so

² "Infinite" in extent relative to the distance between the plate in order to eliminate edge effects.

279 that the charges on each plate will lie totally on the inside surface and the charge density on each
 280 interior surface is $\sigma = q/A$. Since the effect of one plate on the other has been taken into
 281 account in this case the electric fields do *not* add up and the field between the plates is again
 282

$$283 \quad E = \frac{\sigma}{\epsilon_0 \epsilon}. \quad (2.24)$$

284
 285 The charge density on the outer surface of each plate is zero so that the electric field outside the
 286 plates is also zero. Since eq. (2.6) equates σ to D eq. (2.23) yields $E = D/\epsilon_0 \epsilon$, i.e. eq. (2.12).

287 The capacitance is obtained from the voltage difference $V = E \cdot d$ between the plates
 288 and $q = A\sigma_0$:

$$289 \quad C = \frac{q}{V} = \frac{\sigma_0 A}{Ed} = \frac{\sigma_0 A/d}{\epsilon_0 \epsilon / \sigma_0} = (A/d)(\epsilon_0 \epsilon) = (\epsilon_0 \epsilon / k). \quad (2.25)$$

291 2.2.3.7 Concentric Conducting Cylinders

292 Let the inner and outer radii of two concentric conducting cylindrical plates be a and b ,
 293 respectively, let their equal height be h , and let charges $+q$ and $-q$ be uniformly distributed on
 294 the inside surfaces of each plate. Form a concentric cylindrical Gaussian surface of radius
 295 $a < r < b$ and height h , so that $\oint_S \vec{E} \cdot d\vec{A} = E(2\pi r h) = q/\epsilon_0 \epsilon$. Then $E = q/(2\pi r h \epsilon_0 \epsilon)$ so that

$$296 \quad V = \int_a^b E dr = \left(\frac{q}{2\pi h \epsilon_0 \epsilon} \right) \int_a^b \frac{dr}{r} = \frac{q}{2\pi h \epsilon_0 \epsilon} \ln \left(\frac{b}{a} \right) \quad (2.26)$$

299 and the capacitance is

$$300 \quad C = \frac{q}{V} = \frac{2\pi h \epsilon_0 \epsilon}{\ln(b/a)} \quad (2.27)$$

303 2.2.3.8 Concentric Conducting Spheres

304 Let the inner and outer radii of two concentric spherical conducting plates be a and b ,
 305 respectively, and let charges $+q$ and $-q$ reside on the inside surfaces of each plate. Form a
 306 concentric spherical Gaussian surface of radius $a < r < b$, so that $\oint_S \vec{E} \cdot d\vec{A} = E[4\pi r^2] = q/\epsilon_0$
 307 and $E = q/[4\epsilon_0 \pi r^2]$. Then

$$308 \quad V = \int_a^b E dr = \frac{q}{4\pi \epsilon_0 \epsilon} \int_a^b \frac{dr}{r^2} = \frac{q}{4\pi \epsilon_0 \epsilon} \left(\frac{1}{b} - \frac{1}{a} \right) = \frac{q}{4\pi \epsilon_0 \epsilon} \left(\frac{a-b}{ab} \right) \quad (2.28)$$

311
312 and

$$313 \quad C = \frac{q}{V} = 4\pi\epsilon_0\epsilon \left(\frac{ab}{b-a} \right). \quad (2.29)$$

314
315 2.2.3.9 Isolated Sphere

316 The capacitance of an isolated sphere is obtained from eq. (2.29) by taking the limit
317 $b \rightarrow \infty$ and for convenience placing $a = R$:

$$318 \quad C = 4\pi\epsilon_0\epsilon R. \quad (2.30)$$

320
321 Thus larger spheres have larger capacitances.

322
323 2.2.4 Electrostatics

324 Consider a constant voltage V applied across two parallel plates between which there is
325 now a conducting medium. Let the resistivity of the material be $\rho = R.k^{-1}$ (units ohm-meter) and
326 specific conductivity $\sigma = 1/\rho$ (units S m⁻¹), where R is the resistance between the plates in ohms
327 and the symbol S refers to the SI unit Siemen defined as the reciprocal of the ohm. The current
328 density \vec{J} is the electric current per unit (orthogonal) area (units A m⁻²) so that $\vec{J}\rho = \vec{E}$.
329 Unfortunately the displacement current $dD/dt = d\sigma_0/dt$ (better named as the displacement
330 current density) has no symbol.

331 Electric current, symbol I , is defined as

$$332 \quad I \equiv \frac{dq}{dt} \quad (2.31)$$

334
335 so that the total charge that passes across a plane through which a current I flows is

$$336 \quad q = \int_0^t I dt'. \quad (2.32)$$

338
339 The electric potential φ_E is not defined for electrostatics (see §2.5 below on Maxwell's
340 equations) and is replaced by the symbol voltage V (unfortunately also used for the unit volt).
341 Ohm's Law for the electrical resistance R (SI unit ohm (Ω)) is then

$$342 \quad R \equiv \frac{V}{I} \quad (2.33)$$

344
345 and $\Omega = V/A$. An electrical conductor is said to be ohmic if, and only if, R is constant. This is
346 not the same as $dV/dI = \text{constant}$: for example if $V = 1.0 + 2I$ and $dV/dI = 2$ then
347 $R = 3\Omega$ for $I = 1A$, $R = 2.5\Omega$ for $I = 2A$, $R = 2.3\Omega$ for $I = 3A$.

348 Resistances dissipate power P given by $P = IV$ (recall that energy is given by QV and
 349 power is the time derivative of energy). For ohmic resistances

$$\begin{aligned}
 350 \quad P &= IV \\
 351 \quad &= I(IR) = I^2R \\
 &= (V/R)V = V^2/R.
 \end{aligned} \tag{2.34}$$

352 2.2.5 Maxwell's Equations

353 These four equations summarize all that is known about electromagnetic phenomena –
 354 they are essentially the electromagnetic equivalent of Newton's laws for mechanics but more
 355 mathematically sophisticated because of the greater complexity of electromagnetic phenomena.

356 The differential forms of the four Maxwell equations are:

$$357 \quad \vec{\nabla} \cdot \vec{\mathbf{D}} = \rho; \tag{2.35}$$

$$358 \quad \vec{\nabla} \cdot \vec{\mathbf{B}} = 0; \tag{2.36}$$

$$359 \quad \vec{\nabla} \times \vec{\mathbf{E}} = -\left(\frac{\partial \vec{\mathbf{B}}}{\partial t}\right); \tag{2.37}$$

$$360 \quad \vec{\nabla} \times \vec{\mathbf{H}} = \vec{\mathbf{J}} + \left(\frac{\partial \vec{\mathbf{D}}}{\partial t}\right) \tag{2.38}$$

$$361 \quad = \sigma \vec{\mathbf{E}} + \left(\frac{\partial \vec{\mathbf{D}}}{\partial t}\right) \tag{2.39}$$

$$362 \quad = \sigma \vec{\mathbf{E}} + \epsilon_0 \left(\frac{\partial \epsilon \vec{\mathbf{E}}}{\partial t}\right). \tag{2.40}$$

363 For a vacuum equation (2.38) is equivalent to

$$364 \quad \vec{\nabla} \times \vec{\mathbf{B}} = \mu_0 \vec{\mathbf{J}} + \mu_0 \epsilon_0 \left(\frac{\partial \vec{\mathbf{E}}}{\partial t}\right) \tag{2.41}$$

365 where σ is the specific electrical conductivity (units $(\Omega^{-1}\text{m}^{-1} = \text{Sm}^{-1})$), $\vec{\mathbf{B}}$ is the magnetic
 366 induction, and $\vec{\mathbf{H}}$ is the magnetic field. Equations (2.38) - (2.40) merit amplification. The
 367 equation $\vec{\nabla} \times \vec{\mathbf{H}} = \vec{\mathbf{J}}$ might perhaps be expected instead of eq. (2.38) but this has the nonsensical
 368 implication that there could never be any sources or sinks of current anywhere at any time,
 because the vector identity $\vec{\nabla} \cdot (\vec{\nabla} \times \vec{\mathbf{H}}) = 0$ would then imply $\vec{\nabla} \cdot \vec{\mathbf{J}} = 0$. The difficulty is resolved
 by noting that for a charging or discharging parallel plate capacitor (for example) charge flow in
 the external circuit joining the two capacitor plates, corresponding to dq_0/dt where q_0 is the
 charge on the capacitor plates (see §2.1.2 above), must be compensated for by an opposite
 change of the polarization charges between the plates (to ensure charge conservation). Thus

$$379 \quad \vec{\nabla} \cdot (\vec{\nabla} \times \vec{\mathbf{H}}) \equiv 0 = \vec{\nabla} \cdot \left[\left(\frac{\partial q_0}{\partial t} \right) - \left(\frac{\partial q_i}{\partial t} \right) \right] \quad (2.42)$$

380 is ensured.

381 The term $\partial \vec{\mathbf{D}} / \partial t$ in eq. (2.38) can correspond for example to a localized (molecular
382 diameter) effective spatial translation of charge due to rotation of an electric dipole about its
383 center of mass that has a close analogy to an ion hopping to an adjacent site (see §2.2.1.2). It is
384 called the *displacement current*. The term displacement “current” has been claimed to be a
385 misnomer but this is true only if a current is interpreted to be a long range translational migration
386 of charge. If the definition of current as dq/dt is adopted it is not a misnomer because q (on
387 capacitor plates for example) changes with time [eq. (2.42)], and furthermore a traditional
388 current must be present in an external circuit to compensate for $\partial q_i / \partial t$. Describing $\partial \vec{\mathbf{D}} / \partial t$ as a
389 “fictitious current”, as has been done in at least one popular text book, is disingenuous and
390 misleading because eq. (2.38) demonstrates that $\partial \vec{\mathbf{D}} / \partial t$ is just as important in determining a
391 magnetic field as migration of individual charges.

392 The *vector potential* $\vec{\mathbf{A}}$ is defined by

$$393 \quad \vec{\nabla} \times \vec{\mathbf{A}} = \vec{\mathbf{B}} \quad (2.43)$$

394 and
395

$$396 \quad \vec{\mathbf{E}} = -\vec{\nabla} \varphi_E - \frac{\partial \vec{\mathbf{A}}}{\partial t}, \quad (2.44)$$

397
398 and is introduced essentially to ensure consistency between electrostatics and electrodynamics.
399 Equation (2.43) ensures eq. (2.36) because of the vector identity $\vec{\nabla} \cdot (\vec{\nabla} \times \vec{\mathbf{A}}) = 0$ and eqs. (2.43)
400 and (2.44) together ensure that eq. (2.37) remains true in dynamic situations where φ_E is
401 undefined. The vector potential is essentially an extension of the Coulomb potential φ_E to
402 dynamic situations because the definition of φ_E from $\vec{\mathbf{E}} = \nabla \varphi_E$ [eq. (2.10)] is definable only in
403 static situations, as the following consideration indicates: if $\partial \vec{\mathbf{B}} / \partial t \neq 0$ then $\vec{\nabla} \times \vec{\mathbf{E}} \neq 0$ by eq.
404 (2.36) and the static relation

$$405 \quad \vec{\mathbf{E}} = \vec{\nabla} \varphi_E \quad (2.45)$$

406
407
408 could then never hold because of the vector identity $\vec{\nabla} \times (\vec{\nabla} \varphi_E) = 0$. But $\vec{\mathbf{E}}$ is known to be
409 nonzero in dynamic situations (Ohm’s Law!). Similarly if $\vec{\mathbf{J}} \neq 0$ or $\partial \vec{\mathbf{D}} / \partial t \neq 0$ then there is
410 no potential φ_B for $\vec{\mathbf{B}}$ (defined by $\vec{\mathbf{B}} = \vec{\nabla} \varphi_B$) because eq. (2.38) then implies
411
412

413 $\vec{\nabla} \times \vec{\mathbf{H}} = \vec{\nabla} \times \vec{\mathbf{B}} / \mu\mu_0 \neq 0$ because of the same vector identity $\vec{\nabla} \times (\vec{\nabla} \varphi_B) = 0$. Both these
 414 difficulties are averted by the introduction of $\vec{\mathbf{A}}$. Equation (2.44) is then consistent with eq.
 415 (2.37) since it guarantees

$$417 \quad \vec{\nabla} \times \vec{\mathbf{E}} = \vec{\nabla} \times \left(-\vec{\nabla} \varphi_E - \frac{\partial \vec{\mathbf{A}}}{\partial t} \right) = -\frac{\partial \vec{\mathbf{B}}}{\partial t}. \quad (2.46)$$

418
 419 Integral versions of Maxwell's equations include Faraday's Law:

$$421 \quad \oint \vec{\mathbf{E}} \cdot d\vec{\mathbf{s}} = -\frac{d\Phi_B}{dt}; \quad \Phi_B \equiv \oint \vec{\mathbf{B}} \cdot d\vec{\mathbf{A}} = \text{magnetic flux} \quad (2.47)$$

422
 423 and Ampere's law

$$425 \quad \oint \vec{\mathbf{B}} \cdot d\vec{\mathbf{s}} = \mu_0 \epsilon_0 \frac{d\Phi_E}{dt} + \mu_0 I_{\text{enclosed}}; \quad \Phi_E \equiv \oint \vec{\mathbf{E}} \cdot d\vec{\mathbf{A}} = \text{electric flux} \quad (2.48)$$

426
 427 Equation (2.40) provides a convenient means for demonstrating the equivalence of the
 428 complex permittivity and complex conductivity. First convert eq. (2.40) from a vector equation
 429 to a complex scalar equation:

$$431 \quad \vec{\nabla} \times \vec{\mathbf{H}} = \sigma \vec{\mathbf{E}} + \epsilon_0 \left(\frac{\partial \epsilon \vec{\mathbf{E}}}{\partial t} \right) \Rightarrow |\vec{\nabla} \times \vec{\mathbf{H}}| = \sigma^* E^* + \epsilon_0 \epsilon^* \left(\frac{\partial E^*}{\partial t} \right). \quad (2.49)$$

432
 433 For a sinusoidal excitation $E^* = E_0 \exp(-i\omega t)$ eq. (2.49) becomes

$$434 \quad \begin{aligned} |\vec{\nabla} \times \vec{\mathbf{H}}| &= \sigma^* E_0 \exp(-i\omega t) - \epsilon_0 \epsilon^* E_0 (i\omega) \exp(-i\omega t) \\ 435 \quad &= [\sigma^* - i\omega \epsilon_0 \epsilon^*] E_0 \exp(-i\omega t) \\ &= [\epsilon^* - \sigma^* / (i\omega \epsilon_0)] (-i\omega) E_0 \exp(-i\omega t), \end{aligned} \quad (2.50)$$

436
 437 indicating that both the complex conductivity $[\sigma^* - i\omega \epsilon_0 \epsilon^*]$ and complex permittivity
 438 $[\epsilon^* - \sigma^* / (i\omega \epsilon_0)]$ provide equivalent descriptions of electrical relaxation, as do the resistivity
 439 $\rho^* = 1/\sigma^*$ and electric modulus $M^* = 1/\epsilon^*$. All these different functions emphasize or
 440 suppress different facets of experimental data in the same way that Fourier transforms do for
 441 example [see eq. (2.106) below].

442 443 2.2.6 Electromagnetic Waves

444 The Maxwell equations together with the constitutive relations $\vec{\mathbf{D}} = \epsilon_0 \epsilon \vec{\mathbf{E}}$ and $\vec{\mathbf{B}} = \mu_0 \mu \vec{\mathbf{H}}$
 445 predict transverse electromagnetic (em) waves traveling at the speed of light c/n

446

$$447 \quad \frac{c}{n} = \frac{(1/\epsilon_0\mu_0)^{1/2}}{(\epsilon\mu)^{1/2}} = \frac{1}{(\epsilon_0\epsilon\mu_0\mu)^{1/2}}, \quad (2.51)$$

448

449 where

450

$$451 \quad n = (\epsilon\mu)^{1/2} \quad (2.52)$$

452

453 is the refractive index. In a nonmagnetic material for which $\mu = 1$ and $\epsilon^* = (n^*)^2$

454

$$455 \quad (n^*)^2 = (n' - in'')^2 = (n'^2 - n''^2) - 2in'n'' = \epsilon^* = \epsilon' - i\epsilon'' \quad (2.53)$$

456

457 so that

458

$$459 \quad \epsilon' = n'^2 - n''^2 \quad (2.54)$$

460 and

461

$$462 \quad \epsilon'' = 2n'n''. \quad (2.55)$$

463

464 For the general case of a magnetic material where the relative magnetic permeability is also
465 complex, $\mu^* = \mu' - i\mu''$,

466

$$467 \quad (n^*)^2 = (n'^2 - n''^2) - 2in'n'' = (\epsilon' - i\epsilon'')(\mu' - i\mu'') \quad (2.56)$$

468

469 so that

470

$$471 \quad (n^*)^2 = (n'^2 - n''^2) - 2in'n'' = (\epsilon' - i\epsilon'')(\mu' - i\mu'') = (\epsilon'\mu' - \epsilon''\mu'') - i(\epsilon'\mu'' + \epsilon''\mu'), \quad (2.57)$$

472

473 and

474

$$475 \quad n'' = (\epsilon'\mu'' + \epsilon''\mu'). \quad (2.58)$$

476

477 Thus absorption of electromagnetic energy by magnetically lossy materials is enhanced by a high
478 relative permittivity.479 The electric field component of a plane electromagnetic traveling wave of angular
480 frequency ω propagating in the $+x$ direction in a medium with refractive index n and speed c/n
481 is

$$482 \quad E(x, t) = E_0 \exp\left\{-i\omega\left[t - \frac{nx}{c}\right]\right\}, \quad (2.59)$$

483
484 and similarly for the magnetic field component. For complex $n^* = n' - in''$ eq. (2.59) becomes
485

$$\begin{aligned}
 E(x,t) &= E_0 \exp \left\{ -i\omega \left[t - \frac{(n' - in'')x}{c} \right] \right\} \\
 &= E_0 \exp \left\{ -i\omega \left[t - \frac{n'x}{c} \right] \right\} \exp \left[\frac{-n''\omega x}{c} \right]
 \end{aligned}
 \tag{2.60}$$

487
488 so that E decays exponentially with distance $+x$ into the medium. The intensity $I = |E|^2$ of em
489 waves is then
490

$$\begin{aligned}
 I &= E_0^2 \exp \left\{ -2i\omega \left[t - \frac{(n' - in'')x}{c} \right] \right\} \\
 &= E_0^2 \exp \left\{ -2i\omega \left[t - \frac{n'x}{c} \right] \right\} \exp \left[\frac{-2n''\omega x}{c} \right]
 \end{aligned}
 \tag{2.61}$$

492
493 that is to be compared with Beer's Law

$$I = I_0 \exp(-\alpha x), \tag{2.62}$$

496
497 where α is the extinction coefficient (usually expressed in neper m^{-1} where the dimensionless
498 neper is used to emphasize that the logarithmic form of eq. (2.62) implies the Napierian
499 logarithm). Equations (2.61) and (2.62) yield

$$\alpha(\omega) = \frac{2\omega n''(\omega)}{c}. \tag{2.63}$$

502
503 Observe the sign convention for imaginary numbers mentioned in the Introduction of
504 Chapter One at work here. If the sinusoidal perturbation was defined as
505 $E(x,t) = E_0 \exp\{+i\omega[t - nx/c]\}$ and the sign of the imaginary component of ε^* remained
506 negative then α would have to be negative and Beer's Law would predict unphysical
507 exponential growth through a medium. This can be resolved by making the imaginary
508 component of ε^* positive but this corresponds to a dipole rotation that leads the excitation
509 voltage rather than lags it. Nonetheless this is the convention used by electrical engineers and is
510 the price paid for the "advantage" of having a positive sign in the complex exponential. An
511 excellent account of phase conventions is given in Chapter One of ref. [2].

512 Insertion of eq. (2.55) into eq. (2.63) yields

513

$$514 \quad \alpha(\omega) = \frac{\omega \varepsilon''(\omega)}{n'(\omega)c}, \quad (2.64)$$

515

516 and since $\varepsilon'' = \sigma' / (e_0 \omega)$ then

517

$$518 \quad \alpha(\omega) = \frac{\sigma'(\omega)}{n'(\omega)e_0c}. \quad (2.65)$$

519 Thus n'' , ε'' , α and σ' are all measures of absorption of electrical energy:

$$520 \quad \alpha = \frac{\sigma'}{ne_0c} = \frac{\omega \varepsilon''}{nc} = \frac{2\omega n''}{c}. \quad (2.66)$$

521

522 Ordinary em radiation comprises randomly distributed directions of polarization for the
 523 \vec{E} and \vec{B} fields. Radiation for which the direction of polarization is constant and the same for all
 524 waves is said to be polarized. Reflected em waves are partially polarized in the direction parallel
 525 to the reflecting surface, the extent of polarization depending on the angle of incidence.
 526 Polaroid® sun glasses are polarized in the vertical direction and therefore more strongly
 527 attenuate reflected waves. Reflected em waves are fully polarized at the Brewster incident angle.

528

529 2.2.7 Local Electric Fields

530 The electric field inside a dielectric medium is not equal to the applied field because of
 531 electrostatic screening by the medium. This is a complicated problem that is well described in
 532 Chapter One of ref. [3] (by N. E. Hill) and has been considered by Onsager [4], Kirkwood [5],
 533 and Frohlich [6]. The complexity is exemplified by the Kirkwood relation between the isolated
 534 molecular dipole moment μ_g observed in the gas phase and the relative permittivity ε_0^E

535

$$536 \quad \frac{4\pi N g \mu_g^2}{9k_B T V e_0} = \frac{(\varepsilon_0^E - \varepsilon_\infty^E)(2\varepsilon_0^E + \varepsilon_\infty^E)}{\varepsilon_0^E (\varepsilon_\infty^E + 2)}, \quad (2.67)$$

537

538 where ε_∞^E is the limiting high frequency relative permittivity that for a pure dielectric equals the
 539 square of the (limiting low frequency) refractive index n^2 , N is the number of dipoles in a volume
 540 V , and g is a correlation factor that corrects for nonrandom orientations of surrounding dipoles
 541 caused by direction dependent intermolecular forces. The latter is in principle calculable:

542

$$543 \quad g = 1 + \sum_{i \neq j}^N \langle \cos(\theta_{ij}) \rangle \quad (2.68)$$

544

545 where the averaged cosine $\langle \cos(\theta_{ij}) \rangle$ of the angle θ_{ij} between dipoles μ_i and μ_j can be
 546 computed for specific orientation geometries.

547 The treatment of local field effects on the kinetics of dipole relaxation is even more

548 intricate because the reaction field produced by polarization of the dielectric medium by the
 549 embedded dipole is in general out of phase with the applied field. These effects have been
 550 discussed by Mountain [7]. A particularly important effect for relaxation phenomenology is that
 551 a single macroscopic dielectric relaxation time corresponds to two microscopic times. After a
 552 heated debate in the literature the accepted microscopic dipole correlation function is the Fatuzzo
 553 and Mason [8] expression
 554

$$\begin{aligned}
 \varphi(t) &= \left(1 + \frac{\epsilon_\infty}{2\epsilon_0}\right)^{-1} \left[\exp\left(-\frac{t}{\tau_E}\right) + \left(\frac{\epsilon_\infty}{2\epsilon_0}\right) \exp\left(-\frac{\epsilon_0}{\epsilon_\infty} \frac{t}{\tau_E}\right) \right] \\
 &= \left(1 + \frac{\epsilon_\infty}{2\epsilon_0}\right)^{-1} \left[\exp\left(-\frac{t}{\tau_E}\right) + \left(\frac{\epsilon_\infty}{2\epsilon_0}\right) \exp\left(-\frac{t}{\tau_D}\right) \right]
 \end{aligned}
 \tag{2.69}$$

556 where τ_E and τ_D are again the relaxation times for polarization at constant E and D respectively.
 557 Fulton [9] has given a detailed discussion of this subject in which he deduced that the
 558 longitudinal part of polarization relaxes with a time constant τ_D and that the transverse
 559 component relaxes with a time constant τ_E . Electrical relaxation is therefore discussed later in
 560 this chapter in two parts - dielectric relaxation and conductivity relaxation.
 561

562 2.2.8 Circuits

563 There are the four fundamental elements in analog passive circuits: resistance R ;
 564 capacitance C ; self inductance L ; mutual inductance M .

565 2.2.8.1 Simple Circuits

566 *Resistances in Series and in Parallel*

567 For resistances R_s connected in series, the same current I_s must pass through each and the
 570 sum of the voltages across each resistor equals the applied voltage V . Thus
 571 $V = \sum V_i = IR_s = I \sum R_i$ and the equivalent series resistance is

$$R_s = \sum R_i . \tag{2.70}$$

574 For resistances R_p connected in parallel the same voltage V must occur across each and
 575 the total current I through the parallel circuit is the sum of the currents through each:
 576 $I = \sum I_i = \sum V/R_i$ and the equivalent parallel resistance R_p is given by

$$1/R_p = \sum 1/R_i . \tag{2.71}$$

578
 579
 580
 581

582 *Capacitances in Series and in Parallel*

583 Capacitance C is defined as $C \equiv q/V$, where V is the voltage across the capacitor and
 584 $\pm q$ are the charges on each of its ends. For capacitances C_i connected in parallel the same voltage
 585 V must occur across each and the total charge q on each side of the equivalent parallel
 586 capacitance C_p must equal the sum of charges q_i on each component. Thus $q = C_p V = V \sum_i C_i$ and

587 the equivalent parallel capacitance C_p is given by

$$588$$

$$589 \quad C_p = \sum_i C_i . \quad (2.72)$$

590

591 For capacitances connected in series the total voltage V across the series circuit equals
 592 the sum of voltages across each capacitor. The magnitude of the charges q on each must be the
 593 same (since no charge separation can occur across the short circuit joining them) so that
 594 $V = q/C_s = \sum_i V_i = \sum_i q/C_i$ and the equivalent series capacitance C_s is given by

$$595$$

$$596 \quad \frac{1}{C_s} = \sum_i \frac{1}{C_i} . \quad (2.73)$$

597

598 *Inductances in Series and in Parallel*

599 The self-inductance L is defined as $L \equiv V / (dI / dt)$ where V is the voltage across the
 600 device and I is the current through it. Since V is in the numerator and I is in the denominator L
 601 is an impedance akin to R . Impedances add in series so the equivalent series inductance is

$$602$$

$$603 \quad L_s = \sum_i L_i \quad (2.74)$$

604 and since admittances add in parallel the equivalent parallel inductance is

$$605$$

$$606$$

$$607 \quad \frac{1}{L_s} = \sum_i \frac{1}{L_i} \quad (2.75)$$

608

609 The mutual inductance M of a device is defined as $M \equiv V_2 / (dI_1 / dt)$, where V_2 is the
 610 voltage induced on one side of the device by a time varying current I_1 in the other. Mutual
 611 inductances are usually insignificant in relaxation instrumentation since they only occur in
 612 analog instruments that use transformers that are rarely (never?) used now. Rearrangement of the
 613 definition of M yields

$$614$$

$$615 \quad V_2 = M (dI_1 / dt), \quad (2.76)$$

616

617 so that V_2 is smaller at lower frequencies when dI_1/dt is smaller. This is why transformer arm
618 (essentially ac Wheatstone) bridges were useless at low frequencies.

619

620 *Combined Series and Parallel Elements*

621 Consider two examples of a general circuit in which an element Z_1 is in parallel with a
622 series combination of two elements Z_2 and Z_3 . If these elements are resistances R_1 , R_2 and R_3 then
623 $R_{23}=R_2+R_3$ and

624

$$625 \frac{1}{R_{equiv}} = \frac{1}{R_1} + \frac{1}{R_2 + R_3} = \frac{R_1 + R_2 + R_3}{R_1(R_2 + R_3)} \quad (2.77)$$

626

627 or

628

$$629 R_{equiv} = \frac{R_1(R_2 + R_3)}{R_1 + R_2 + R_3}. \quad (2.78)$$

630

631 If these elements are capacitances C_1 , C_2 and C_3 then
632 $1/C_{23} = 1/C_2 + 1/C_3 \Rightarrow C_{23} = C_2 C_3 / (C_2 + C_3)$ and

633

$$634 C_{equiv} = C_1 + C_{23} = C_1 + \frac{C_2 C_3}{C_2 + C_3} = \frac{C_1 C_2 + C_2 C_3 + C_3 C_1}{C_2 + C_3}. \quad (2.79)$$

635

636 2.2.8.2 AC Circuits

637 If the applied voltage is $V(t) = V_0 \cos(\omega t) = \text{Re}[V_0 \exp(-i\omega t)]$ the average voltage over
638 one period is zero but the ac power is not. Equation (2.34) indicates that power is determined by
639 the averages of I^2 and V^2 that are both proportional to the averages of $\sin^2(\omega t)$ or $\cos^2(\omega t)$ over
640 one cycle that are both equal to $1/2$. Thus

641

$$642 P_{average} = (V_0^2 / 2) R = I_0^2 R / 2. \quad (2.80)$$

643

644 The ac power dissipation is therefore given by the same relation for DC power dissipation if the
645 maximum ac voltage (V_0) and current (I_0) are replaced by $V_0 / \sqrt{2}$ and $I_0 / \sqrt{2}$ respectively. The
646 latter are referred to as rms (root mean square) voltages and currents. Electrical outlet ac voltages
647 such as 120V in North America are given as rms values; the peak voltage in North America is
648 therefore $(120V)(2)^{1/2} = 170V$.

649 AC impedances $Z^*(i\omega)$ are defined as $V^*(i\omega) / I^*(i\omega)$ and ac admittances $A^*(i\omega)$

650 as $I^*(i\omega) / V^*(i\omega)$. The imaginary components of $A^*(i\omega)$ and $Z^*(i\omega)$ are referred to as

651 reactances, and as shown below do not dissipate power.

652

653 *Resistances*654 For a voltage $V = V_0 \exp(-i\omega t)$ applied across a resistance R the current is

655

$$656 \quad I_R(i\omega t) = \frac{V(i\omega t)}{R} = \frac{V_0}{R} \exp(-i\omega t) = V_0 G \exp(-i\omega t) \quad (2.81)$$

657 so that the impedance is

658

$$659 \quad Z_R^*(i\omega t) = \frac{V^*(i\omega t)}{I^*(i\omega t)} = \frac{V_0 \exp(-i\omega t)}{(V_0/R) \exp(-i\omega t)} = R \quad (2.82)$$

660

661 and the admittance $A_R^*(i\omega t) = 1/Z_R^*(i\omega t) = G$ where G is the conductance. Both R and G are real
662 and independent of frequency.

663

664 *Capacitances*665 For a capacitance C the current is

666

$$667 \quad I_C(i\omega t) = \frac{dq(\omega t)}{dt} = C \frac{dV(i\omega t)}{dt} = V_0 [-i\omega C \exp(-i\omega t)] \quad (2.83)$$

668

669 and the capacitive impedance is

670

$$671 \quad Z_C^*(i\omega t) = \frac{V^*(i\omega t)}{I_C^*(i\omega t)} = \frac{V_0 \exp(-i\omega t)}{V_0 [-i\omega \exp(-i\omega t)]} = \frac{1}{-i\omega C} = \frac{i}{\omega C} \quad (2.84)$$

672

673 and the capacitive admittance is

674

$$675 \quad A_C^*(i\omega t) = -i\omega C. \quad (2.85)$$

676

677 The capacitive admittance and admittance are therefore frequency dependent and imaginary
678 (thus a reactance). Power dissipation per cycle in a capacitance is given by

679

$$\begin{aligned} P_C(t) &= \langle V_C(t) I_C(t) \rangle = \langle [V_0 \exp(-i\omega t)] V_0 [-i\omega C_p \exp(-i\omega t)] \rangle = -V_0^2 \omega C_p \langle \exp(-2i\omega t) \rangle \\ 680 \quad &= \langle -V_0^2 \omega C_p [\cos(-2\omega t) - i \sin(-2\omega t)] \rangle \quad (2.86) \\ &= \langle -V_0^2 \omega C_p [\cos(-2\omega t)] \rangle + \langle i V_0^2 \omega C_p \sin(-2\omega t) \rangle = 0 \end{aligned}$$

681

682 because the averages of both $\cos(2\omega t)$ and $\sin(2\omega t)$ over one cycle are zero. The capacitive
 683 impedance is therefore not a resistance if "resistance" is taken to imply power dissipation. This is
 684 the why an inductive or capacitive impedance is not considered to be an "ac resistance". For the
 685 phase convention adopted here the reactance is capacitive if the imaginary part of the complex
 686 admittance is negative and is inductive if the imaginary part of the complex admittance is
 687 positive.

688
 689 *Inductances*

690 For a self-inductance L the current is
 691

$$692 \quad I_L(\omega t) = \int \left(\frac{V}{L} \right) dt = \int \left(\frac{V_0 \exp(-i\omega t)}{L} \right) dt = \left(\frac{V_0}{L} \right) \frac{\exp(-i\omega t)}{-i\omega} \quad (2.87)$$

693
 694 so that inductive impedance is
 695

$$696 \quad Z_L^*(i\omega t) = \frac{V^*(i\omega t)}{I_L^*(i\omega t)} = -i\omega L \quad (2.88)$$

697
 698 and the inductive admittance is
 699

$$700 \quad A_L^*(i\omega t) = \frac{1}{-i\omega L} = \frac{i}{\omega L} \quad (2.89)$$

701
 702 The inductive reactance is therefore also imaginary and frequency dependent. Power dissipation
 703 in an inductance is given by
 704

$$705 \quad P_L(t) = \langle V_L(t) I_L(t) \rangle = \left\langle \left[V_0 \exp(-i\omega t) \right] \left(\frac{V_0}{L} \right) \frac{\exp(-i\omega t)}{-i\omega} \right\rangle \quad (2.90)$$

$$= -\frac{V_0^2}{-i\omega L} \langle \exp(-2i\omega t) \rangle = \frac{V_0^2}{i\omega L} \langle \exp(-2i\omega t) \rangle = 0.$$

706
 707 Thus the power dissipated by a pure inductance is zero just like that of a capacitance ("pure"
 708 meaning negligible resistance).
 709

710 *Parallel Resistance and Capacitance*

711 Consider a voltage $V = V_0 \cos(\omega t)$ applied across a resistance R_p in parallel with a
 712 capacitance C_p . The current I_R through the resistance is
 713

$$714 \quad I_R = \frac{V}{R_p} = \frac{V_0 \cos(\omega t)}{R_p} = V_0 \cos(\omega t) G_p = \text{Re} \left[V_0 G_p \exp(-i\omega t) \right] \quad (2.91)$$

715
716
717

where $G_p = 1/R_p$ is the conductance. The current through the capacitance I_C is

$$I_C = \frac{dq_C}{dt} = C_p \frac{dV}{dt} = -V_0 \omega C_p \sin(\omega t) \quad (2.92)$$

$$= -V_0 \omega C_p \cos(\omega t - \pi/2) \operatorname{Re}[-iV_0 \omega C_p \exp(-i\omega t)]$$

719

720 where q_C is the charge on the capacitor. Equation (2.92) implies that the sinusoidal
721 (displacement) current I_C lags the applied voltage by $\pi/2$ radians because
722 $\sin(\omega t) = \cos(\omega t - \pi/2)$. The total current through the parallel $R_p C_p$ circuit is

$$I = I_R + I_C = V_0 G_p \cos(\omega t) - V_0 \omega C_p \sin(\omega t)$$

$$= \operatorname{Re}[V_0 G_p \exp(-i\omega t)] + \operatorname{Re}[-iV_0 \omega C_p \exp(-i\omega t)] \quad (2.93)$$

$$= \operatorname{Re}\{V_0 [G_p - i\omega C_p] \exp(-i\omega t)\}.$$

724 The phase relations for the current are therefore conveniently expressed by defining the parallel
725 combination of resistance and capacitance as a complex admittance A^*

$$A^* = G_p - i\omega C_p, \quad (2.94)$$

727 or as a complex impedance Z^*

$$Z^* = 1/A^* = \frac{1}{G_p - i\omega C_p} = \frac{G_p}{G_p^2 + \omega^2 C_p^2} + \frac{i\omega C_p}{G_p^2 + \omega^2 C_p^2}. \quad (2.95)$$

729 The complex capacitance is

$$C^* = \frac{A^*}{-i\omega} = C_p + \frac{iG_p}{\omega} \quad (2.96)$$

731 and the complex electric modulus is

$$M^*(i\omega) = 1/C^*(i\omega) = i\omega Z^*(i\omega). \quad (2.97)$$

733 Equation (2.95) is equivalent to

$$Z^* = \frac{R_p}{1 + \omega^2 \tau_D^2} + \frac{iR_p \omega \tau_D}{1 + \omega^2 \tau_D^2} \quad (2.98)$$

735 where

$$\tau_D = R_p C_p \quad (2.99)$$

737 is the Maxwell relaxation time (the reason for the subscript D is given below).

738 When normalized by the cell constant k (dimensions m^{-1}) the quantities A^* , Z^* and C^*
739 become respectively the complex conductivity $\sigma^* = kA^*$, complex resistivity $\rho^* = Z^*/k$, and
740 complex relative permittivity $\varepsilon^* = kC^*/\epsilon_0 = C^*/C_0$ where C_0 is the capacitance of the
741 measuring cell in a vacuum (usually equated to that in air).

742 The reciprocal of $\varepsilon^*(i\omega)$ is the complex electric modulus

743

$$744 \quad M^*(i\omega) \equiv \frac{1}{\varepsilon^*(i\omega)} \quad (2.100)$$

745
746 so that
747

$$748 \quad M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}; M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}. \quad (2.101)$$

749
750 *Series Resistance and Capacitance*

751 For a resistance R_s in series with a capacitance C_s

$$753 \quad Z^*(i\omega) = R_s + \frac{1}{i\omega C_s} = R_s - \frac{i}{\omega C_s} = R_s \left(\frac{\omega\tau_E - i}{\omega\tau_E} \right), \quad (2.102)$$

$$755 \quad A^*(i\omega) = \frac{R_s}{1 + \omega^2 R_s^2 C_s^2} + \frac{i\omega R_s^2 C_s}{1 + \omega^2 R_s^2 C_s^2} = \frac{R_s}{1 + \omega^2 \tau_E^2} + \frac{i\omega R_s \tau_E}{1 + \omega^2 \tau_E^2}, \quad (2.103)$$

$$757 \quad C^*(i\omega) = \frac{A^*(i\omega)}{-i\omega} = C_s \left(\frac{1 - i\omega R_s C_s}{1 + \omega^2 R_s^2 C_s^2} \right) = C_s \left(\frac{1}{1 + \omega^2 \tau_E^2} - \frac{i\omega\tau_E}{1 + \omega^2 \tau_E^2} \right), \quad (2.104)$$

$$759 \quad M^*(i\omega) = \frac{1}{C^*(i\omega)} = \frac{-i\omega}{A^*(i\omega)} = -i\omega Z^*(i\omega) = -i\omega \left[R_s - \frac{i}{\omega C_s} = R_s \left(\frac{\omega\tau_E - i}{\omega\tau_E} \right) \right] \\ = \frac{-R_s}{\tau_E} (1 + i\omega\tau_E) \quad (2.105)$$

760
761 where $\tau_E \equiv R_s C_s$ and is not generally equal to $\tau_D \equiv R_p C_p$.

762 The relations between the four response functions are conveniently summarized by [1,10]
763

$$764 \quad \begin{array}{ccc} \varepsilon^*(i\omega) & \Leftrightarrow & 1/M^*(i\omega) \\ \Downarrow & & \Downarrow \\ \sigma^*(i\omega)/(ie_0\omega) & \Leftrightarrow & ie_0\omega/\rho^*(i\omega) \end{array} \quad (2.106)$$

765
766 2.2.8.3 Experimental Factors
767 *Cable Effects*

768 Cable impedances can be analyzed using transmission line techniques that invoke an
769 infinite number of $\{L, C\}$ components. One line of the cable is considered to be a series of
770 inductances L and the other line as a zero impedance wire, with capacitances C connecting the

771 two between every pair of inductances. In the limit of an infinite number of inductance and
 772 capacitance elements the cable impedance is $Z_{cable} = (L/C)^{1/2}$ and is real and constant. Coaxial
 773 cables are made so that C is 30 pF/ft and L is 0.075 μH /ft so that
 774 $Z_{cable} = (7.5 \times 10^{-8} H / 3.0 \times 10^{-11})^{1/2} = 50 \Omega$. Thus a short cable with a 50Ω resistor across it looks
 775 like an infinitely long cable and a 50Ω load on the cable has an ideal impedance match for
 776 maximum power transfer (see electrical engineering texts). Such a cable will also behave as an
 777 inductor if short circuited so that for a high conductivity attached sample resonance effects may
 778 be significant.

779 *Electrode Polarization*

781 This occurs for two and three terminal measurements when charge transfer does not
 782 occur between an electrode and the sample material, i.e. when the applied voltage is less than the
 783 decomposition potential of the sample (four terminal measurements are immune to this but they
 784 do not produce reliable capacitance data and require separate sample preparation). In this case
 785 the contact can be approximated as a large capacitance C_s in series with the sample [11-13]. If
 786 the amplitude of the applied potential is too large (above the decomposition potential of the
 787 electrolyte) a Faradaic impedance [14, 15] will also occur in parallel with this capacitance [16]
 788 that can sometimes be approximated as a Warburg impedance.

789 A series capacitance does not affect $M''(\omega)$ and simply adds $1/C_s$ to $M'(\omega)$: the total
 790 impedance $Z_{total}^*(i\omega)$ of the sample impedance $Z^*(i\omega)$ and C_s is
 791 $Z_{total}^*(i\omega) = Z^*(i\omega) + 1/i\omega C_s$ so that

$$792$$

$$793 M^*(i\omega) = i\omega Z_{total}^* = i\omega Z^*(i\omega) + 1/C_s. \quad (2.107)$$

794
 795 It is a considerable advantage of the electric modulus function that $M''(\omega)$ is unaffected by
 796 electrode polarization and other high capacitance phenomena. This is exploited in some of the
 797 methods of data analysis discussed below but it is noted that this advantage is not shared by the
 798 imaginary component of the resistivity ρ'' because

$$799$$

$$800 \lim_{\omega \rightarrow 0} \rho''(\omega) \propto \lim_{\omega \rightarrow 0} \left(\frac{1}{k \omega C_s} \right) = \infty. \quad (2.108)$$

801
 802 The low frequency behavior of ρ' can be useful (see below). Electrode polarization can make
 803 the direct determination of the low frequency quantities ϵ_0 and σ_0 difficult and sometimes
 804 impossible because it increases ϵ' above ϵ_0 at low frequencies and, usually at lower
 805 frequencies, decreases σ' to below σ_0 . Overlap between bulk relaxations and these two
 806 electrode polarization effects often prevents the observation of limiting low frequency plateaus in
 807 $\epsilon'(\omega)$ and/or $\sigma'(\omega)$. Although relaxation of electrode polarization occurs at lower frequencies
 808 than the bulk relaxation,

809

$$810 \quad \tau_{electrode} = \frac{\epsilon_0 C_s}{C_0 \sigma_0} \gg \frac{\epsilon_0 C_p}{C_0 \sigma_0} = \tau_D, \quad (2.109)$$

811

812 the magnitude of the polarization dispersion can be very large [proportional to $(C_s - C_p) \approx C_s$]

813 and its high frequency tail can extend well into the bulk relaxation region. This phenomenon is

814 illustrated by the following representative average circuit quantities: a parallel capacitance

815 $C_p = 10$ pF and parallel resistance $R_p = 10^7$ ohm in series with a polarization capacitance of

816 $C_s = 10^4$ pF. Because both R_p and C_p will have distributions in a typical electrolyte there will be

817 dispersions in both ϵ' and σ' . The dispersion is centered around $\omega \approx 1/(R_p C_p) = 10^4$ s⁻¹ and

818 the low frequency plateau in ϵ' would normally be seen at ca. $\omega \approx 10^2$ s⁻¹, but this is dwarfed by

819 the polarization capacitance at that frequency, $C'_{pol}(\omega \gg (R_p C_s)^{-1}) = C_s / (\omega^2 R_p^2 C_s^2) = 100$ pF,

820 an order of magnitude higher than C_p . On the other hand, the low frequency dispersion in

821 conductivity due to polarization has barely begun at $\omega = 10^2$:

822 $\sigma_{ele} / \sigma_0 = \omega^2 \tau_{ele}^2 / (1 + \omega^2 \tau_{ele}^2) = 0.99$ for $\omega \tau_{ele} = \omega R_p C_s = (10^2)(10^{-1}) = 10$, where the fact

823 that the limiting high frequency conductivity for the Debye-like relaxation of electrode

824 polarization is σ_0 :

825

$$826 \quad \lim_{\omega \tau_{ele} \rightarrow \infty} \sigma'_{ele} = \frac{(\epsilon_0 - \epsilon_\infty)_{ele} e_0}{\tau_E} = \frac{(\epsilon_0 - \epsilon_\infty)_{ele} e_0 \epsilon_\infty}{\tau_D \epsilon_0} = \frac{(\epsilon_0 - \epsilon_\infty)_{ele} \sigma_0}{\epsilon_0} \approx \sigma_0 \text{ for } \epsilon_{0,ele} \gg \epsilon_{\infty,ele} \quad (2.110)$$

827

828 Effects similar to electrode polarization can arise from other causes, such as poor electrode

829 contact where a capacitance due to air gaps occurs in parallel with a resistance at the contact

830 areas. Poor contacts have been shown to give spurious dielectric losses in un-doped alkali halides

831 [17], and is suspected to be responsible for the poor reproducibility of other dielectric data for

832 alkali halides [18]. Space charge effects can also produce a series capacitance at the electrode

833 [19,20].

834

835 2.3 Dielectric Relaxation

836 An excellent resource for dielectric relaxation that is ref. [3], particularly Chapter One by

837 N. E. Hill. An excellent review of dielectric relaxation phenomena in supercooled and glassy

838 materials is given by Richert [21] that also includes references to modern measurement

839 technology.

840

841 2.3.1 Frequency Domain

842 2.3.1.1 Dipole Rotation

843 A freely rotating dipole in a sinusoidally varying electric field with an angular frequency

844 ω low enough that the dipole can keep up with the field behaves as a pure capacitance C_{pure} .

845 The current then lags the field by $\pi/2$ radians and the complex admittance is

$$846 \quad 847 \quad A^* = i\omega C_{pure}. \quad (2.111)$$

848
849 If the dipole cannot keep up with the field because of friction with its environment it will lag by
850 an additional angle δ and a component of the current appears in phase with the voltage and is
851 measured as a resistance. Thus eq. (2.92) is replaced by

$$852 \quad I_C = -V_0\omega C_p \cos(\omega t - \pi/2 - \delta)$$

$$853 \quad = -V_0\omega C_p [\cos(\omega t - \pi/2)\cos\delta + \sin(\omega t - \pi/2)\sin\delta] \quad (2.112)$$

$$= -V_0\omega C_p [\sin(\omega t)\cos\delta - \cos(\omega t)\sin\delta]$$

854
855 and the term $+V_0\omega C_p \cos(\omega t)\sin\delta$ in eq. (2.112) is indeed in phase with the applied voltage
856 $V = +V_0 \cos(\omega t)$. Note that this in-phase component is zero when $\delta = 0$. Comparing eq. (2.112)
857 with eqs. (2.93) and (2.94) reveals that

$$858 \quad 859 \quad A^* = \omega C_{pure} \sin\delta + i\omega C_{pure} \cos\delta \quad (2.113)$$

860
861 And

$$862 \quad 863 \quad C^* = C' - iC'' = C_{pure} \cos\delta - iC_{pure} \sin\delta \quad (2.114)$$

864
865 so that

$$866 \quad 867 \quad G_p(\text{effective}) = \omega C_{pure} \sin\delta \quad (2.115)$$

868
869 and

$$870 \quad 871 \quad C_p(\text{effective}) = C_{pure} \cos\delta. \quad (2.116)$$

872 Note that at low frequencies when the lag angle δ tends to zero the effective capacitance equals
873 C_{pure} and $G_p = 0$ as must be. When normalized by the geometric capacitance associated with the
874 cell constant k , $C_0 = \epsilon_0 / k$ where ϵ_0 is the vacuum permittivity 8.854×10^{-12} F m⁻¹, the complex
875 capacitance becomes the complex permittivity, $\epsilon^* = C^*/C_0$ so that

$$876 \quad 877 \quad \epsilon^* = \epsilon' - i\epsilon'' \quad (2.117)$$

878
879 where

880

$$881 \quad \varepsilon' = \frac{C_p}{C_0} (\varepsilon_0 - \varepsilon_\infty) \cos(\delta) + \varepsilon_\infty, \quad (2.118)$$

$$882 \quad \varepsilon'' = \frac{G_p}{\omega \cdot C_0} = \frac{\sigma}{e_0 \cdot \omega} = \frac{C_p}{C_0} (\varepsilon_0 - \varepsilon_\infty) \sin(\delta), \quad (2.119)$$

883

884 and

885

$$886 \quad \tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{G_p}{\omega C_p}. \quad (2.120)$$

887

888 Note that $\tan \delta$ is independent of the geometric capacitance C_0 and has the same frequency889 dependence as ε'' but with a retardation time of $(\varepsilon_\infty^E / \varepsilon_0^E)^{1/2} \tau_E$ rather than τ_E . Equations (2.113)

890 and (2.114) imply

$$891 \quad A^* = i\omega C_0 \varepsilon^* \quad (2.121)$$

892 so that

$$893 \quad \sigma^* = kA^* = i\omega \varepsilon_0 \varepsilon^* \quad (2.122)$$

894 and

$$895 \quad \rho^* = \frac{1}{\sigma^*} = \frac{1}{i\omega \varepsilon_0 \varepsilon^*} \quad (2.123)$$

896 The complex electric modulus M^* is defined as the reciprocal of ε^* :

$$897 \quad M^* = 1 / \varepsilon^* \quad (2.124)$$

898 so that

899

$$900 \quad M^* = i\omega C_0 Z^* = i\omega \varepsilon_0 \rho^* \quad (2.125)$$

901

902 The functions σ^* , ε^* , ρ^* and M^* are all analytical and their components all conform to the
903 Cauchy-Riemann and Kronig-Kramers equations.904 For a single relaxation time the (Debye) functions $\varepsilon^*(i\omega)$, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for
905 dielectric relaxation are

$$906 \quad \varepsilon^*(i\omega) = \varepsilon_\infty^E + \frac{(\varepsilon_0^E - \varepsilon_\infty^E)}{1 + i\omega\tau_E}, \quad (2.126)$$

$$907 \quad \varepsilon'(\omega) = \varepsilon_\infty^E + \frac{(\varepsilon_0^E - \varepsilon_\infty^E)}{1 + \omega^2\tau_E^2}, \quad (2.127)$$

908 and

$$909 \quad \varepsilon''(\omega) = \frac{(\varepsilon_0^E - \varepsilon_\infty^E)\omega\tau_E}{1 + \omega^2\tau_E^2}, \quad (2.128)$$

910 where ε_0^E and ε_∞^E are defined in §2.1.1 as the limiting low and high frequency limits of $\varepsilon'(\omega)$
 911 respectively. Equations (2.127) and (2.128) yield a complex plane plot of ε'' vs ε' that is a
 912 semicircle centered on the real axis at $\varepsilon' = (\varepsilon_0^E + \varepsilon_\infty^E)/2$. This is found by eliminating $\omega\tau_E$
 913 between equations (2.127) and (2.128).

914 The corresponding Debye functions for $\sigma'(\omega)$ and $\sigma''(\omega)$ are

$$915 \quad \sigma'(\omega) = e_0 \omega \varepsilon''(\omega) = \frac{e_0 (\varepsilon_0^E - \varepsilon_\infty^E) \omega^2 \tau_E}{1 + \omega^2 \tau_E^2} \quad (2.129)$$

916 and

$$917 \quad \sigma''(\omega) = e_0 \omega \varepsilon_\infty^E + \frac{e_0 \omega (\varepsilon_0^E - \varepsilon_\infty^E)}{1 + \omega^2 \tau_E^2}. \quad (2.130)$$

918 Thus the real part of the conductivity of a Debye dielectric increases from zero at low
 919 frequencies to a high frequency limit of
 920

$$921 \quad \sigma_\infty = \lim_{\omega \rightarrow \infty} \sigma'(\omega) = e_0 (\varepsilon_0^E - \varepsilon_\infty^E) / \tau_E \quad (2.131)$$

922 and the imaginary part diverges at high frequencies. Derivations of the Debye expressions for
 923 $M'(\omega)$ and $M''(\omega)$ are instructive and straightforward but tedious – they are given in Appendix
 924 2.1. The results are
 925

$$926 \quad M'(\omega) = M_0^D + \frac{(M_\infty^D - M_0^D) \omega^2 \tau_D^2}{1 + \omega^2 \tau_D^2} \quad (2.132)$$

927 and

$$928 \quad M''(\omega) = \frac{(M_\infty^D - M_0^D) \omega \tau_D}{1 + \omega^2 \tau_D^2}, \quad (2.133)$$

929 where $M_0^D = 1/\varepsilon_0^D$, $M_\infty^D = 1/\varepsilon_\infty^D$, and $(\varepsilon_\infty^D / \varepsilon_0^D) \tau_E = \tau_D$.

930 If a limiting low frequency conductivity σ_0 is present that is not physically related to the
 931 dielectric loss process (e.g. ionic conductivity in a dilute aqueous solution), it must be subtracted
 932 from the measured conductivity before the dielectric loss is calculated from eq. (2.128).
 933 Otherwise the limiting low frequency dielectric loss $\lim_{\omega \rightarrow 0} \varepsilon'' \rightarrow 0$ will be masked by the rapid rise
 934 from the conductivity contribution
 935

$$936 \quad \lim_{\omega \rightarrow 0} \varepsilon'' = \lim_{\omega \rightarrow 0} \frac{\sigma_0}{e_0 \omega} \rightarrow \infty. \quad (2.134)$$

940
 941 It has been argued that this subtraction is physically meaningful only if the conductivity is
 942 unrelated to the dielectric loss process (as in the aqueous solutions mentioned above, for
 943 example). If the dielectric loss peak correlates with σ_0 as occurs in alkali silicate glasses [22-28]
 944 then the subtraction of σ_0 can be regarded as artificial and other methods of data analysis are
 945 preferred (although this position is not universally accepted). This is the principle reason for not
 946 using the complex permittivity in analyzing highly conducting materials and is the subject of
 947 §2.4.

948 If the decay function is nonexponential dielectric relaxation can be described in terms of
 949 a distribution of retardation times $g(\ln \tau_E)$ defined by the relations

$$951 \quad \phi_E(t) = \int_{-\infty}^{+\infty} g(\ln \tau_E) \exp\left(-\frac{t}{\tau_E}\right) d \ln \tau_E \quad (2.135)$$

952 and

$$953 \quad \int_{-\infty}^{+\infty} g(\ln \tau_E) d \ln \tau_E = 1 \quad (2.136)$$

954 so that eq. (2.126) generalizes to

$$957 \quad \varepsilon^* - \varepsilon_\infty^E = (\varepsilon_0^E - \varepsilon_\infty^E) \int_{-\infty}^{+\infty} \frac{g(\ln \tau_E)}{1 + i\omega\tau_E} d \ln \tau_E. \quad (2.137)$$

958 The generalization of eqs. (2.127) and (2.128) are

$$961 \quad \varepsilon'(\omega) = \varepsilon_\infty^E + (\varepsilon_0^E - \varepsilon_\infty^E) \left[\int_{-\infty}^{\infty} g(\ln \tau_E) \frac{1}{1 + \omega^2 \tau_E^2} d \ln \tau_E \right] = \varepsilon_\infty^E + (\varepsilon_0^E - \varepsilon_\infty^E) \left\langle \frac{\omega\tau_E}{1 + \omega^2 \tau_E^2} \right\rangle \quad (2.138)$$

962 and

$$963 \quad \varepsilon''(\omega) = (\varepsilon_0^E - \varepsilon_\infty^E) \int_{-\infty}^{\infty} g(\ln \tau_E) \frac{\omega\tau_E}{1 + \omega^2 \tau_E^2} d \ln \tau_E = (\varepsilon_0^E - \varepsilon_\infty^E) \left\langle \frac{\omega\tau_E}{1 + \omega^2 \tau_E^2} \right\rangle. \quad (2.139)$$

964 The n^{th} moments of a distribution function are

$$967 \quad \langle \tau_E^n \rangle = \int_{-\infty}^{+\infty} \tau_E^n g(\ln \tau_E) d \ln \tau_E. \quad (2.140)$$

968

969 If the integral $\int_{-\infty}^{+\infty} g(\ln \tau_E) d \ln \tau_E$ diverges, as it does for a constant phase angle impedance for
 970 example, $g(\ln \tau_E)$ is not renormalizable and a constant phase angle impedance can therefore be
 971 valid only over a limited range in relaxation times. In terms of $\phi(t)$ the moments are
 972

$$973 \quad \langle \tau_E^n \rangle = \frac{1}{\Gamma(\omega)} \int_0^{+\infty} t^{n-1} \phi(t) dt \quad (2.141)$$

974
 975 and
 976

$$977 \quad \langle \tau_E^{-n} \rangle = (-1)^n \left[\frac{d^n (\phi_E)}{dt^n} \right]_{t=0} \quad (2.142)$$

978
 979 2.3.1.2 Ionic Hopping

980 Chapter One of [3] by N. E. Hill discusses the studies of Frohlich [6] and others on the
 981 dielectric relaxation consequences of two state models. We select here the Frohlich account of an
 982 entity that has only two possible equilibrium positions 1 and 2. The entity could be a molecular
 983 dipole or an ion for example. If the transition probabilities between the two positions are w_{12} and
 984 w_{21} when there is no applied field then a Debye relaxation with a single relaxation time
 985 $\tau_E = 1/(w_{12} + w_{21})$ is predicted that has an Arrhenius temperature dependence
 986 $\tau_E = A \exp(\Delta H / RT)$ where the pre-exponential factor A is a weak function of temperature and
 987 ΔH is the energy barrier that separates the two positions. As noted by Hill, however, a
 988 nonexponential decay function may result from local field effects.

989
 990 2.3.2 Time Domain

991 Consider the case where an electric field E is "instantaneously" increased from zero to E_0
 992 across a dielectric sample at time $t = t'$ and kept constant thereafter, i.e. $E(t) = E_0 h(t')$ where
 993 $h(t)$ is the Heaviside function (see eq. (1.327) in Chapter One). The initially randomized dipoles
 994 will partially orient themselves over time and the polarization and displacement will both
 995 increase (the final average orientation will not be complete because of thermal fluctuations):

$$996 \quad D(t) = D(0) + [D(\infty) - D(0)][1 - \phi_E(t)], \quad (2.143)$$

997
 998 where $D(0)$ and $D(\infty)$ are the limiting short time (high frequency) and long time (low
 1000 frequency) values of $D(t)$ and $\phi_E(t)$ is the decay function for polarization at constant E
 1001 corresponding to $D(t)$. The increase of D from zero to $D(\infty)$ is "instantaneous" compared with
 1002 dielectric relaxation times (generally no shorter than about 10^{-11} s) and is due to polarization of
 1003 molecular electron clouds that occurs roughly on optical time scales.

1004 It is sometimes convenient to approximate the relation between time domain data and

1005 $\varepsilon''(\omega)$ by the *Hamon approximation*

1006

$$1007 \quad \varepsilon''(\omega) \approx (\varepsilon_0^E - \varepsilon_\infty^E) \left(\frac{-d\phi_E}{dt} \right) \left(\frac{5t}{\pi} \right), \quad (2.144)$$

1008

1009 obtained from the simplification that the normalized displacement current is given by

1010

$$1011 \quad \left(\frac{-d\phi_E}{dt} \right) \sim t^{-n}. \quad (2.145)$$

1012

1013 No comparably simple relation exists between $\varepsilon'(\omega)$ and $\phi(t)$. Williams, Watt, Dev and North

1014 [29] have shown that for the Williams-Watt [30] decay function

1015

$$1016 \quad \phi(t) = \exp \left[- \left(\frac{t}{\tau_0} \right)^\beta \right] \quad (2.146)$$

1017

1018 the Hamon approximation is accurate within 1% for $\omega\tau_0 > 1$ but fails for $\omega\tau_0 \leq 1$ and $\beta > 0.2$.

1019 Equation (2.144) therefore offers a high frequency approximation to the frequency domain

1020 Williams-Watt function that cannot be expressed in terms of named functions.

1021 The complex relative permittivity $\varepsilon^*(\omega)$ is related to the derivative of $\varepsilon(t)$ by

1022

$$1023 \quad \varepsilon^*(i\omega) - \varepsilon_\infty^E = (\varepsilon_0^E - \varepsilon_\infty^E) \int_0^\infty \left(\frac{d\phi_E}{dt} \right) \exp(-i\omega t) dt \quad (2.147)$$

1024

1025 where $\varepsilon_0 = D(\infty)/E_0$ and $\varepsilon_\infty = D(0)/E_0$. In the simplest case $\phi_E(t)$ is exponential,

1026

$$1027 \quad \phi_E(t) = \exp \left[- \left(\frac{t}{\tau_E} \right) \right] \quad (2.148)$$

1028

1029 and insertion of eq. (2.148) into eq. (2.147) yields the Debye equations (2.127) and (2.128)

1030 [Chapter One of ref. 3].

1031

1032 2.3.3 Temperature Domain

1033 In many situations ω and τ_E are approximately interchangeable variables. Since τ_E

1034 often varies strongly with temperature a narrow temperature range can be used as a surrogate for

1035 a wide frequency range. The temperature dependence of τ_E is approximated over small ranges in
 1036 temperature T by the Arrhenius relation

$$1037 \quad \tau = \tau_0 \exp\left(\frac{E_a}{RT}\right), \quad (2.149)$$

1038 where τ_0 is independent of temperature, R is the ideal gas constant, and E_a is the activation
 1039 energy. Thus the variables $\ln(\omega\tau)$ at constant ω and E_a/RT are equivalent for a single
 1040 relaxation time dielectric. In this case eq. (2.149) indicates that over the convenient temperature
 1041 range from liquid nitrogen (77 K) to room temperature (300K) the retardation time can vary over
 1042 a very large range. For example τ changes by a factor of 10^{25} for an activation energy of 50
 1043 kJ/mol. The temperature variable is therefore extremely useful for scans of the total relaxation
 1044 spectrum and is frequently used for polymers whose relaxation behavior is typically
 1045 characterized by widely separated and very broad relaxation processes. Activation energies E_a
 1046 are obtained from plots of log frequency $\ln f$ against the inverse temperature $1/T_{\max}$ at which ε''
 1047 or $\tan \delta$ passes through its maximum:
 1048

$$1049 \quad \left\langle \frac{E_a}{R} \right\rangle = - \left[\frac{d \ln f}{d(1/T)} \right]. \quad (2.150)$$

1050
 1051 It has been reported [32] that the activation energy obtained in this way is ambiguous because it
 1052 depends on whether the derivative is determined in the isothermal frequency domain or in the
 1053 temperature domain at constant frequency: the frequency domain plot of $\ln f_{\max}$ vs. $1/T$ was found
 1054 to be strongly curved whereas the plot of $\ln f$ vs. $1/T_{\max}$ was found to be linear.

1055 Although temperature is useful because of its experimental convenience it is not
 1056 quantitative because essentially everything changes with temperature. For example the
 1057 dispersion $(\varepsilon_0^E - \varepsilon_\infty^E)$ can only be estimated because both ε_0^E and to a much less extent ε_∞^E are
 1058 temperature dependent. The dispersion $(\varepsilon_0^E - \varepsilon_\infty^E)$ can be estimated from the relation [33]
 1059

$$1060 \quad (\varepsilon_0^E - \varepsilon_\infty^E) \approx \left(\frac{2}{\pi R} \right) \left\langle \frac{1}{E_a} \right\rangle^{-1} \int_0^\infty \varepsilon''(T) d(1/T) \quad (2.151)$$

1061 but this is approximate because of two assumptions in its derivation that must be made for
 1062 mathematical tractability: (i) $(\varepsilon_0^E - \varepsilon_\infty^E)$ is independent of temperature [32] and (ii) $\langle E_a \rangle = \langle 1/E_a \rangle^{-1}$
 1063 that is not generally true because of the Schmidt inequality (Chapter One)
 1064
 1065

$$1066 \quad \langle E_a \rangle \langle 1/E_a \rangle^{-1} \geq 1. \quad (2.152)$$

1067
 1068 The approximation is clearly better for smaller temperature ranges. There are two situations
 1069 where $\ln \omega$ and E_a/RT are not even approximately equivalent: (i) functions for which ω and τ_E

1070 are not invariably multiplied together (for example the conductivity of a Debye dielectric, eq.
1071 (2.128)); (ii) distributions of retardation times that change with temperature.

1072

1073 2.3.4 Equivalent Circuits

1074 The electrical response for an exponential dielectric decay function, the Debye relations
1075 eqs. (2.127) and (2.128) plus any separate conductivity contribution σ_E , is simulated by an
1076 equivalent circuit comprising three parallel arms: a capacitance C_p , a series combination of R_s
1077 and C_s , and a resistance R_p . The relaxation part of the circuit is the series component $R_s + C_s$,
1078 the parallel resistance R_p corresponds to the separate conductivity and the parallel capacitance
1079 C_p simulates the limiting high frequency permittivity. If for a particular range of frequencies the
1080 equivalent circuit of an experimental sample resembles $R_s + C_s$ and the frequency range
1081 encompasses $\omega = 1/(R_s C_s)$ then a dielectric loss peak will be observed in that frequency range.
1082 An example is electrode polarization in a conducting medium that at low frequencies is
1083 approximated by an electrode capacitance in series with the low frequency resistance of the
1084 sample. In this case a dielectric loss is observed with a retardation time given by the product of
1085 the polarization capacitance and sample resistance. Electrode polarization effects in solid
1086 electrolytes can often be a serious problem and are discussed in §2.3.6.1 and §2.3.6.4 below.

1087 In terms of the equivalent circuit the components of the complex permittivity are (see
1088 Appendix 2.3)

1089

$$1090 \quad \varepsilon'(\omega) = \frac{\sigma''}{\varepsilon_0 \omega} = \left(\frac{1}{C_0} \right) \left(C_p + \frac{C_s}{1 + \omega^2 \tau_E^2} \right) \quad (2.153)$$

1091

1092 and

1093

$$1094 \quad \varepsilon''(\omega) = \frac{\sigma'}{\varepsilon_0 \omega} = \left(\frac{C_s}{C_0} \right) \left(\frac{\omega \tau_E}{1 + \omega^2 \tau_E^2} \right) + \frac{\sigma_0}{\varepsilon_0 \omega}. \quad (2.154)$$

1095

1096 that reproduce the Debye relations eqs. (2.127) and (2.128). The low and high frequency limits
1097 of ε' are

1098

$$1099 \quad \lim_{\omega \rightarrow 0} \varepsilon'(\omega) = \varepsilon_0 = \left(\frac{C_p + C_s}{C_0} \right) \quad (2.155)$$

1100

1101 and

1102

$$1103 \quad \lim_{\omega \rightarrow \infty} \varepsilon'(\omega) = \varepsilon_\infty = \left(\frac{C_p}{C_0} \right). \quad (2.156)$$

1104

1105 Matlab®/GNUOctave codes for computing $M^*(i\omega)$ and $\rho^*(i\omega)$ with the added R_p are given in
 1106 Appendix 2.2. A notable result is that $M^*(i\omega)$ exhibits two relaxations corresponding to the
 1107 Debye relaxation and an additional relaxation due to σ_0 . The Debye relaxation for $M^*(i\omega)$ is
 1108 unaffected by R_p but the conductivity relaxation due to σ_0 is.

1109 The occurrence of a dielectric and conductivity relaxation together raises an important
 1110 nomenclature issue that has produced much confusion: the subscripts for denoting limiting low
 1111 and high frequency limits can be ambiguous because these limits can refer to either the average
 1112 dielectric relaxation frequency or to the average conductivity relaxation frequency. In particular,
 1113 the quantity ε_∞ that enters into the expression for the conductivity relaxation time,
 1114 $\langle \tau_D \rangle = e_0 \varepsilon_\infty / \sigma_0$, is the *high* frequency limit for the *conductivity* relaxation, that may correspond
 1115 to the *low* frequency limit for a separate dielectric relaxation. A proposed nomenclature to
 1116 resolve this ambiguity was given above in §2.1.

1117 The “absolute” high frequency limits $\omega \rightarrow \infty$ and $\omega \rightarrow 0$, rather than
 1118 $\{\omega\tau_E, \omega\tau\} \rightarrow \infty, 0$ are

$$1119 \lim_{\omega \rightarrow 0} M' = \frac{\varepsilon_\infty^E \omega^2 \tau_E^2}{(\varepsilon_\infty^E)^2 \omega^2 \tau_E^2} \rightarrow \frac{1}{\varepsilon_\infty^E} \quad (\text{independent of } \sigma_0) \quad (2.157)$$

1121 and
 1122
 1123

$$1124 \lim_{\omega \rightarrow \infty} M'' = \frac{\omega\tau_E (\varepsilon_0^E - \varepsilon_\infty^E) + \sigma_0 \tau_E / e_0}{(\varepsilon_\infty^E)^2 \omega^2 \tau_E^2} \rightarrow 0 \quad (\text{independent of } \sigma_0) \quad (2.158)$$

1125 2.3.5 Interfacial Polarization

1126 In a homogeneous material $\vec{\nabla} \cdot \vec{\mathbf{D}} = e_0 \varepsilon \vec{\nabla} \cdot \vec{\mathbf{E}} = 0$ implies $\vec{\nabla} \cdot \vec{\mathbf{E}} = 0$. At the interface between
 1127 two dielectric materials of different permittivity, however, there is a discontinuity in ε and
 1128 $\vec{\nabla} \cdot \vec{\mathbf{D}} = 0$ no longer implies $\vec{\nabla} \cdot \vec{\mathbf{E}} = 0$. The solution to this problem is obtained by applying
 1129 Gauss’s and Stokes’ theorems to the interface with the result that the tangential component of $\vec{\mathbf{E}}$
 1130 is continuous across the interface and the normal component of $\vec{\mathbf{D}}$ is either continuous (no
 1131 interfacial charge) or discontinuous if there is a free charge (not the result of polarization of the
 1132 materials on each side of the interface). These boundary conditions make interfacial effects
 1133 dependent on the geometry of the interface.

1134 Relaxation of interfacial polarization between alternating slabs of insulating dielectric
 1135 and conducting layers, generically referred to as a *Maxwell Layered Dielectric*, is characterized
 1136 by a single relaxation time τ_i given by
 1137
 1138

$$\tau_i = R_s C_s = \left(\frac{\ell_R}{\ell_C} \right) \epsilon_0 \rho \epsilon = \left(\frac{\ell_R}{\ell_C} \right) \left(\frac{\epsilon_0 \epsilon}{\sigma} \right) \quad (2.159)$$

1140
1141 where ℓ_R is the thickness of the resistive layer with material resistivity ρ and ℓ_C is the
1142 thickness of the capacitive layer with material permittivity ϵ .

1144 2.3.6 Maxwell-Wagner Polarization

1145 Relaxation of interfacial polarization between a conducting sphere embedded in a
1146 dielectric continuum is known as *Maxwell-Wagner (MW) polarization*. Wagner [34] computed
1147 the observed loss tangent ($\tan \delta$) for a volume fraction ϕ of spheres of material conductivity σ_1
1148 and relative permittivity ϵ_1 suspended in a dielectric medium of relative permittivity ϵ_2 , that was
1149 then generalized by Sillars [35] to suspensions of nonspherical particles. An excellent discussion
1150 of the phenomenon is given in ref [3] from which much of the following is distilled. We also
1151 draw from the paper by van Beek [36] who gave the Sillars formula and then considered the
1152 special case of suspended spheres, and noted that the often cited Wagner formula is only correct
1153 when the permittivities of the suspended material and the dielectric medium are equal and that
1154 the Sillars expression does not have this flaw.

1155 The Sillars expression is

$$\tan \delta = \frac{\epsilon_2 K}{\left[\epsilon_\infty (\epsilon_2 K + \epsilon_\infty) \right]^{1/2}} \left(\frac{\omega \tau_0}{1 + \omega^2 \tau_0^2} \right) \quad (2.160)$$

1158
1159 with
1160

$$\begin{aligned} K &= \frac{n^2 \phi \epsilon_2}{\left[(n-1) \epsilon_2 + \epsilon_1 \right]}; \\ \epsilon_\infty &= \epsilon_2 \left[1 + \frac{n \phi (\epsilon_2 - \epsilon_1)}{(n-1) \epsilon_2 + \epsilon_1} \right]; \\ T &= \frac{\epsilon_0 \left[(n-1) \epsilon_2 + \epsilon_1 \right]}{\sigma_1}; \\ \tau_0 &= \frac{T}{\left\{ (\epsilon_1 K + \epsilon_\infty) / \epsilon_\infty \right\}^{1/2}}, \end{aligned} \quad (2.161)$$

1162
1163 where a is parallel to the field direction and n is a function of the aspect ratio a/b of the
1164 suspended particles. The limiting values for n are
1165

$$\begin{aligned}
& n \sim 1 && (a < b) && (a) \\
1166 \quad & n = 3 && (a = b) && (b) && (2.162) \\
& n \approx \left\{ \frac{a^2}{b^2 [\ln(2a/b) - 1]} \right\} && (a > b) && (c)
\end{aligned}$$

1167
1168 Equation (2.162)(c) indicates that for needle-like particles oriented in the direction of the field
1169 the value of n can be large – for example $n \sim 50$ for $a = 10b$. Because $\tan \delta$ is roughly
1170 proportional to n^2 [eqs. (2.160) and (2.161)] the Maxwell-Wagner-Sillars effect can produce very
1171 large dielectric losses. For spherical particles
1172

$$\begin{aligned}
& K = \frac{9\phi\epsilon_2}{[2\epsilon_2 + \epsilon_1]}; \\
1173 \quad & e_\infty = \epsilon_2 \left[1 + \frac{3\phi(\epsilon_2 - \epsilon_1)}{2\epsilon_2 + \epsilon_1} \right]; && (2.163) \\
& T = \frac{e_0 [2\epsilon_2 + \epsilon_1]}{\sigma_1},
\end{aligned}$$

1174
1175 and τ_0 is unchanged. The maximum value of $\tan \delta$ is therefore
1176

$$1177 \quad \tan \delta_{\max} = \frac{\epsilon_2 K}{2[e_\infty (\epsilon_2 K + e_\infty)]^{1/2}}. && (2.164)$$

1178
1179 This expression is inconveniently complicated but simplifies when $\phi \rightarrow 0$:
1180

$$1181 \quad \lim_{\phi \rightarrow 0} (\tan \delta_{\max}) = \frac{9\phi\epsilon_2}{2(2\epsilon_2 + \epsilon_1)} && (2.165)$$

1182
1183 The components of the complex relative permittivity for the Maxwell-Wagner phenomenon
1184 ($\phi \rightarrow 0$) are conveniently expressed using three ancillary functions [36]:
1185

$$1186 \quad \epsilon_\phi = \epsilon_2 \left\{ 1 + \frac{3\phi(\epsilon_1 - \epsilon_2)}{2\epsilon_2 + \epsilon_1} \right\} && (2.166)$$

$$1187 \quad S = \frac{9\phi\epsilon_2}{2\epsilon_2 + \epsilon_1} && (2.167)$$

1189

$$1190 \quad T = \frac{\sigma_1}{\epsilon_0(2\epsilon_2 + \epsilon_1)}. \quad (2.168)$$

1191

1192 Then

1193

$$1194 \quad \epsilon'' = \frac{(\epsilon_\phi S \omega T)}{1 + \omega^2 T^2} \quad (2.169)$$

1195

1196 and

1197

$$1198 \quad \epsilon' = \epsilon_\phi \left\{ 1 + \frac{S}{1 + \omega^2 T^2} \right\}. \quad (2.170)$$

1199

1200 The maximum in the observed dielectric loss ϵ''_{MW} is therefore

1201

$$1202 \quad \epsilon''_{\max} = \frac{9\phi\epsilon_2^2}{2(2\epsilon_2 + \epsilon_1)} \left[1 + \frac{3\phi(\epsilon_2 - \epsilon_1)}{2\epsilon_{12} + \epsilon_1} \right] \rightarrow \frac{9\phi\epsilon_2^2}{2(2\epsilon_2 + \epsilon_1)} \quad (2.171)$$

1203

1204 that occurs at an angular frequency ω_{\max} given by

1205

$$1206 \quad \omega_{\max} = 1/\tau_{MW} = \frac{\sigma_1}{\epsilon_0(2\epsilon_1 + \epsilon_2)}. \quad (2.172)$$

1207

1208 At ω_{\max} the value of ϵ' from eq. (2.170) is $\lim_{\phi \rightarrow 0} \epsilon' = \epsilon_2$ that when combined with eq. (2.171)

1209 produces eq. (2.165).

1210

1211 2.3.7 Examples

1212 Attention is restricted to the dielectric relaxation of water. Emphasis is given to those
1213 techniques that extract information that cannot easily be obtained using the usual formalisms.

1214

1215 2.3.7.1 Liquid Water

1216 Water is one of the few liquids that relaxes with a single retardation time (or very close to
1217 it) and therefore has a Debye complex permittivity. Its dielectric relaxation frequency depends on
1218 temperature but always lies within the microwave region of the *em* spectrum. This has important
1219 implications for both navigational and meteorological radar and is of course the basis for
1220 microwave cooking. The temperature dependence of the retardation time is not Arrhenius but
1221 rather adheres to the empirical Fulcher equation (1.543)

1222

$$1223 \quad \tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \quad (2.173)$$

1224

1225 with parameters $\tau_0 = 1.25 \times 10^{-13}$ s, $B = 669$ K, $T_0 = 138$ K that accurately describes $\tau(T)$ down
 1226 to the limit of supercooling of water, ca. -35°C . The relaxation frequency $(1/2\pi\tau)$ therefore
 1227 varies between 62 GHz at 0°C and 74 GHz at 100°C and the energy absorption at 100°C is
 1228 about 75% that at 0°C . Microwave ovens generally operate at a frequency 2.45 GHz that lies on
 1229 the low frequency side of the Debye dielectric loss peak - the dielectric losses at these
 1230 temperature extremes are about 4.0% and 3.3% of the maximum loss at $(1/2\pi\tau)$ Hz.

1231

1232 2.3.7.2 Supercooled Water

1233

1234

1235

1236

1237

1238

1239

1240

1241

1242

1243

1244

1245

1246

1247

1248

1249

1250

1251

1252

1253

1254

1255

1256

1257

1258

1259

1260

Maxwell-Wagner polarization has been used to obtain the relative permittivity of supercooled water down to about -35°C [37, 38]. The Maxwell-Wagner losses occur in the frequency range $10^5 - 10^6$ Hz that is far below the frequency range for the dielectric relaxation of water (around 10^{10} Hz). Thus the measured values for the relative permittivity of water correspond to the limiting low frequency values $\varepsilon_0 > \sim 80$. This range is also far above the relaxation frequency for ice that is about $10^{3.5}$ Hz at 0°C and decreases with decreasing temperature, so that if crystallization occurred the relevant relative permittivity of ice is the limiting high frequency value $\varepsilon_\infty \sim 5$. It is fortunate that the Maxwell-Wagner losses occur at frequencies between the relaxation frequency ranges of water and ice.

Emulsions of water in heptane stabilized by the surfactant sorbitol tristearate [37] and droplets suspended in beeswax [38] both exhibit Maxwell-Wagner polarization. In the first and rigorous beeswax study by Hasted and Shahidi [38] volume fractions of 0.5% and 1.0% were used. Hodge and Angell [37] later used a much larger volume fraction of water (30%) that was necessitated by their much lower instrumental sensitivity. Their data were stated to be inconsistent with the Maxwell-Wagner formulae because their values of ε''_{\max} were claimed to be about four times larger than predicted and their sign of $(d\varepsilon''_{\max}/dT) \propto (d\varepsilon_1/dT)$ was positive rather than negative as predicted by their eq. (3). However their eq. (3) is incorrect – the numerator term ε_2^2 of eq. (2.171) was given as ε_1^2 so that the analyses of ε''_{MW} given in [1] and [37] are both incorrect. Equation (2.171) predicts that ε''_{\max} is indeed inversely proportional to ε_1 if $\varepsilon_1 \gg \varepsilon_2$ (a good approximation for water droplets in hexane). The analyses in terms of the electric modulus [1,37] are unaffected and remain valid although the stated requirement that a series capacitance that simulates the surfactant layer around the droplet needs to be large for the modulus analysis to be useful [1] is not correct (see eq. (2.107) above).

The observed maxima in ε'' decreased with decreasing temperature that is consistent with eq. (2.171), but for $\varepsilon_1 \approx 100 \gg \varepsilon_2 \approx 2$ and $\phi = 0.3$ the predicted value is about $\varepsilon''_{\max} \approx \{(9)(0.3)(4)/[2(106)]\} \approx 0.005$, compared with the experimental values that range between about 0.4 – 0.8. The predicted value is therefore too large by a factor of about 100. Also, the measured ratio of ε''_{\max} at the temperature extremes of 0°C and -35°C is about 1.8

1261 compared with the correct value of about 1.2. The observed values of ω_{\max} for ε'' were centered
 1262 around $2\pi(5.5 \times 10^6 \text{ Hz}) \approx 3.5 \times 10^7 \text{ rad/s}$ from which eq. (2.172) predicts a conductivity of about
 1263 $\sigma_1 \approx \varepsilon_0 [(2\varepsilon_1 + \varepsilon_2) + \phi(\varepsilon_1 - \varepsilon_2)] \omega_{\max} / (1 - \phi) \approx (9 \times 10^{-12} \text{ F/m})(230)(3.5 \times 10^7) / 0.7$
 1264 $\approx (9 \times 10^{-12} \text{ F/m})(230)(3.5 \times 10^7) / 0.7 \approx 0.1 \text{ S/m}$ that is impossibly high. Thus the observed ε''
 1265 data greatly differ from the Maxwell-Wagner predictions.

1266 The measured modulus peak heights also decreased with decreasing temperature and
 1267 since M_{\max}'' is assumed to be inversely proportional to the permittivity this trend is also in the
 1268 correct direction. Values of ε_1 for water were then derived by assuming that $M_{\max}'' \propto 1/\varepsilon_1$,
 1269 fixing the proportionality constant from literature data for ε_1 at 0 °C and then least squares fitting
 1270 a quadratic in temperature to eight data points between 0 °C and -35 °C. Agreement with the
 1271 earlier results, of which the authors were unaware at the time of paper submission (see *Note*
 1272 *added in Proof* in [37]), was within the $\pm 2\%$ uncertainties claimed for each method but the
 1273 agreement is better than this because most of the discrepancies are systematic due to the different
 1274 values of ε_1 at 0 °C for the two methods (measured in [38] but chosen from the literature as a
 1275 proportionality constant in [37]). When this is corrected for by equating the average of the
 1276 modulus derived permittivities to the average from reference [38] the differences are reduced to
 1277 0.5% or less (column four in Table 1). This is a remarkable result given the simplifications used
 1278 in the modulus analysis.

1279 These results can be rationalized in terms of a simplified equivalent circuit for the
 1280 emulsified water droplets: a parallel ($R_1 C_1$) element corresponding to the water droplet with
 1281 relative permittivity ε_1 and conductivity σ_1 in series with a capacitance C_s , simulating the
 1282 suspected thin layer of interfacial material, and a capacitance C_2 in parallel with the series
 1283 combination corresponding to the surrounding heptane. Intuitively, C_2 is much smaller than C_1
 1284 from both geometrical and physical considerations ($\varepsilon_1 \gg \varepsilon_2$). The circuit analysis is:

1285 (i) Admittance A_1 of parallel ($R_1 C_1$) element:

1286
$$A_1 = 1/R_1 + i\omega C_1 = (1 + i\omega R_1 C_1) / R_1 = (1 + i\omega \tau_1) / R_1 \text{ so that } Z_1 = R_1 / (1 + i\omega \tau_1).$$

1287 (ii) Impedance of $\{(R_1 C_1) + C_s\}$ arm = $Z_{1s} = \frac{R_1}{1 + i\omega \tau_1} + \frac{1}{i\omega C_s} = \frac{i\omega R_1 C_s + 1 + i\omega \tau_1}{i\omega C_s (1 + i\omega \tau_1)}$

1288
$$\Rightarrow A_{1s} = \frac{i\omega C_s (1 + i\omega \tau_1)}{1 + i\omega (\tau_1 + R_1 C_s)}.$$

1289 (iii) Admittance A_{1s2} of complete circuit:

1290
$$A_{1s2} = A_{1s} + i\omega C_2 = \frac{i\omega C_s - \omega^2 C_s \tau_1 + i\omega C_2 [1 + i\omega (\tau_1 + R_1 C_s)]}{1 + i\omega (\tau_1 + R_1 C_s)}$$

1291
$$= \frac{i\omega (C_s + C_2) - \omega^2 (C_s \tau_1 + C_2 \tau_1 - R_1 C_s C_2)}{1 + i\omega (\tau_1 + R_1 C_s)}.$$

1292 (iv) For $C_2 \ll C_1$ appropriate for water droplets in heptane the admittance simplifies to

$$1293 \quad A_{1s2} = \frac{i\omega C_s - \omega^2 R_1 C_1 C_s}{1 + i\omega R_1 (C_1 + C_s)}.$$

1294 Thus

$$1295 \quad C_{1s2}^* = \frac{A_{1s2}}{i\omega} = \frac{C_s (1 + i\omega R_1 C_1)}{1 + i\omega R_1 C_s} = \frac{C_s (1 + i\omega R_1 C_1)(1 + i\omega R_1 C_s)}{1 + \omega^2 R_1^2 C_s^2} \quad (2.174)$$

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

1296 The maximum value of C'' is $(C_1 + C_s)/2$ that is determined in part by the surfactant layer and is
 1297 greater than the value $C_1/2$ for no series capacitance. This is consistent with the observed
 1298 maxima in ε'' [37] being about 100 times greater than that calculated from the Maxwell-Wagner
 1299 expression. The maximum in C'' also occurs at $\omega_{\max} = 1/(R_1 C_s)$ that is determined in part by the
 1300 surfactant layer. The dependency of the relaxation time on C_s can account for the (unreported)
 1301 fact that changing the suspending medium changed ω_{\max} [37] since the suspending medium
 1302 would be expected to affect the surfactant layer and C_s .

1303 The imaginary component of the electric modulus for $C_2 \ll C_1$ is

$$1304 \quad M'' = \frac{i\omega R_1}{(1 + i\omega^2 R_1^2 C_1^2)} = \left(\frac{1}{C_1}\right) \frac{i\omega R_1 C_1}{(1 + i\omega^2 R_1^2 C_1^2)}, \quad (2.175)$$

1305 the maximum value of which is $1/(2C_1)$ and therefore contains the desired information about C_1
 1306 that is independent of C_s . The frequency of maximum M'' is $\omega_{\max} = 1/(R_1 C_1)$ and is also
 1307 independent of C_s . Observe that these simplifications arise solely from making C_2 much smaller
 1308 than C_1 and do not depend on C_s being much larger than C_1 as stated earlier [1].

1309 Matlab® and GNUOctave calculations of the relaxation functions for the circuit enable
 1310 values of the circuit elements to be quickly estimated that produce trends that are generally
 1311 consistent with the experimental data, with the notable exception of the maximum values of ε''
 1312 (discussed briefly below). For example good agreement with the experimental trends is attained
 1313 with $R_1 = 10^3$; $C_1 = 10^{-3}$; $C_2 = 10^{-5}$; $C_s = 5 \times 10^{-4}$. The value of 100 for the ratio C_1/C_2 was
 1314 chosen to approximate the ratio of permittivities of water and hexane and to accommodate an
 1315 unknown geometric factor for the suspending medium relative to the droplet, and the value of C_s
 1316 was found from the experimental ratio of 0.5 for the frequencies of maximum ε'' and M'' (the
 1317 latter being higher). The geometric factor is probably the largest source of uncertainty in the
 1318 values of the circuit parameters.

1319 Equation (2.174) indicates that the maximum value of ε'' should be increased by a factor
 1320 of $(C_1 + C_s)/C_1 \approx 100$ over that for no surfactant, consistent with experiment [37].

1321 The Maxwell-Wagner equivalent circuit discussed here is obviously crude but serves to
 1322 rationalize the remarkable success of the electric modulus in analyzing the Maxwell-Wagner
 1323 effect for water droplets in a dielectric medium of low permittivity.

1324

1325 2.3.7.3 Hydration Water

1326 Water of ionic hydration is readily probed by dielectric relaxation, if the ionic
 1327 conductivity contribution to ε'' and $\tan\delta$ is sufficiently small. Data for glasses of $\text{Ca}(\text{NO}_3)_2$
 1328 hydrates [39] provide a convenient illustration of how water in different environments can be
 1329 distinguished dielectrically. Spectra of dielectric $\tan\delta$ vs. $1/T$ at 1 Hz were shown for eight
 1330 glasses of composition $\text{Ca}(\text{NO}_3)_2 \cdot R\text{H}_2\text{O}$ $\text{Ca}(\text{NO}_3)_2 \cdot R\text{H}_2\text{O}$ ($R = 3, 4, 5, 6, 8, 10, 12, 14$).
 1331 Glasses with lower R values required the addition of KNO_3 to ensure glass formation but this
 1332 was expected to have only a minor effect on water dynamics because of the larger ionic
 1333 charge/radius of K^+ compared with Ca^{2+} . Four relaxations were observed:

1334 (α) A conductivity relaxation at low $1/T$ corresponding to the glass transition manifested as
 1335 the steep increase in $\tan\delta$. The relaxation temperature corresponds to $\tan\delta = 1$ (*vide infra*) and
 1336 will be referred to as the "conductivity wing". It is essential that this relaxation occur at
 1337 sufficiently high T in order that the other relaxations occur in the poorly conducting glassy state
 1338 and not be hidden beneath the conductivity contribution to $\tan\delta$.

1339 (β) A dielectric relaxation lying close to the conductivity wing whose shift in position with R
 1340 paralleled that of the conductivity relaxation. It was observable only as a shoulder for $R = 1-6$
 1341 and (probably) $R = 10$ but is seen as a clear peak for $R \approx \text{trace}$.

1342 (γ) A weak low temperature dielectric relaxation ($\tan\delta_{\text{max}} \approx 10^{-3} - 10^{-2}$) in the
 1343 $\text{Ca}(\text{NO}_3)_2 \cdot R\text{H}_2\text{O}$ system occurred as a broad maximum for $R = 4, 5, 6$ and as a shoulder for
 1344 $R \geq 8$.

1345 (δ) A dielectric relaxation whose intensity increased rapidly with R . It is probably a part of
 1346 the broad maximum near $10^3/T \approx 7.5$ for $R = 8$ but appeared as a clear maximum for $R \geq 10$.

1347 The β relaxation was assigned to cation bound water that presumably coordinates Ca^+
 1348 rather than K^+ because of the larger ionic charge/radius ratio of the former. The rapid shift in
 1349 relaxation temperature with $R > 1$ was interpreted as a change in water dynamics as H_2O replaces
 1350 NO_3^- in the first coordination shell of Ca^+ . The R - invariance for $R = \text{trace}$ and $R = 1$ was
 1351 attributed to a single water molecule lying in the first coordination shell. This assignment of the
 1352 β relaxation to Ca^{2+} bound water implied a dielectric activity that merits discussion. The most
 1353 plausible geometry for H_2O coordinated to Ca^+ is when the H_2O dipole points away from the
 1354 Ca^+ ion. However if this held in the complex ionic environment of the glass there would be no
 1355 dielectric activity because the rotational axis would bisect the H-O-H angle and coincide with
 1356 the dipole vector. Two alternatives suggest themselves:

1357 (1) Exchange of water and nitrate in the coordination shell. This implies an associated
 1358 volume fluctuation and ultrasonic activity. Such activity has been observed [40,41] in
 1359 $\text{Ca}(\text{NO}_3)_2 \cdot R\text{H}_2\text{O}$ solutions at about 20 MHz at room temperature. This relaxation moved to
 1360 higher frequencies with increasing R and the edge of a second relaxation at higher frequencies
 1361 was noted, both being consistent with the glassy state dielectric behavior. Such an exchange
 1362 would also be expected to contribute to the translational ionic migration that produces
 1363 conductivity, consistent with the essentially R - invariant difference between the α and β

1364 relaxation temperatures. The possibility that this relaxation is part of a conductivity relaxation
1365 with a distribution of relaxation times is discussed in §2.5.

1366 (2) A different $\text{Ca}^+ \text{-OH}_2$ geometry is favored in which the dipole vector and rotation axis do
1367 not coincide. Neutron diffraction data indicate this occurs in CaCl_2 and NiCl_2 solutions [42], in
1368 which an angle of ca. 40° was observed between the dipole and coordination axes at $R = 12.6$
1369 (NiCl_2) and 12.3 (CaCl_2), and about 0° in dilute solutions ($R \approx 450$). It was not possible to
1370 find the dielectric activity per water molecule of the β relaxation in the $\text{Ca}(\text{NO}_3)_2 \cdot \text{RH}_2\text{O}$
1371 glasses because of overlap with the conductivity wing and the γ relaxation, but for the mixed
1372 nitrate glasses the well-defined conductivity wing for the anhydrous mixture could be shifted and
1373 subtracted to yield plausibly shaped peaks of $\tan \delta$ vs. $1/T$. The peak heights and widths in the
1374 $R = 1$ and $R = 3$ glasses were about the same so that barring an unlikely ratio of activation
1375 energies in excess of 3 it appears that the dielectric activity per water molecule does indeed
1376 decrease with increasing R . A crude calculation indicated that the observed values of $\tan \delta_{\text{max}}$
1377 yielded sensible values of $\Delta\theta$. The dipole being relaxed was assumed to be the component of
1378 the water dipole (μ_w) orthogonal to the rotation axis, magnitude $\mu_w \sin(\Delta\theta)$, and $\tan \delta_{\text{max}}$ was
1379 assumed to be proportional to $(\epsilon_0 - \epsilon_\infty)$ that is in turn proportional to $R[\mu_w \sin(\Delta\theta)]^2$. Equating
1380 $\tan \delta_{\text{max}}$ for the $1R$ and $3R$ glasses then yielded

$$1381 \quad \frac{3}{T_{3R}} \sin^2(\Delta\theta_{3R}) = \frac{1}{T_{1R}} \sin^2(\Delta\theta_{1R}), \quad (2.176)$$

1382 so that

$$1383 \quad \sin^2(\Delta\theta_{3R}) \approx 0.286 \sin^2(\Delta\theta_{1R}). \quad (2.177)$$

1384 Examples of $\{\Delta\theta_{1R}, \Delta\theta_{3R}\}$ pairs were $\{60^\circ, 28^\circ\}$ and $\{30^\circ, 15^\circ\}$, both of which were sensible
1385 values and roughly comparable with the neutron diffraction values.

1386 For large values of R the δ relaxation was expected to resemble pure water so that an
1387 extrapolation to infinite dilution should yield the temperature at which the relaxation frequency
1388 of water is 1 Hz. The retardation temperatures at 1 Hz for the δ relaxation in four aqueous
1389 glasses (solutions of $\text{Ca}(\text{NO}_3)_2$, CaZnCl_4 , Li_2ZnCl_4 and ZnCl_2) all extrapolated to about 162 ± 5
1390 K at infinite dilution, strongly suggesting that the relaxation temperature for pure water would be
1391 162 ± 5 K at 1 Hz. The temperature dependence of the relaxation time for water between -20°C to
1392 $+30^\circ\text{C}$ [43] was found to follow the Fulcher equation

$$1393 \quad \tau(T) = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \quad (2.178)$$

1394 with $A = 1.25 \times 10^{-13}$ s, $B = 669$ K, $T_0 = 138$ K. The extrapolated {1 Hz, 162 ± 5 K} datum
1395 agreed with the Fulcher value {1 Hz, 162 K} (uncertainties not stated). Given the large
1396 extrapolation over about 11 orders of magnitude this agreement constitutes strong evidence that
1397 dielectric relaxation of water outside the first coordination shell of the Ca^{2+} and Li^+ cations is the
1398 same as pure water. A similar extrapolation of LiCl in glycerol data yields a relaxation
1399 temperature equal to the directly observable value for pure glycerol at 1 Hz.

1400

1401 2.4 Conductivity Relaxation

1402 2.4.1 General Aspects

1403 As noted earlier relaxation of polarization can occur either by translation of electric
 1404 charge (electric current) or by dipole rotation (displacement current). Thus polarization induced
 1405 by an electric field can occur by *conductivity relaxation* [44] arising from long range
 1406 translational migration of point charges as well as by the dielectric relaxation considered so far
 1407 (dipole rotation or localized hopping of ions between sites). The time scale associated with a
 1408 frequency invariant conductivity σ_0 defined by

$$1409 \quad \langle \tau_D \rangle = \sigma_0 / e_0 \epsilon_\infty \quad (2.179)$$

1410 (see eq. 1.42 Chapter One), but this time scale is not evident in σ' vs $\ln \omega$ plots nor is it for the
 1411 monotonic function $\epsilon^* = \epsilon' - i\sigma_0 / e_0 \omega$. However ρ'' and M'' clearly indicate the time scale
 1412 because they exhibit maxima in the frequency domain at $\omega \approx 1 / \langle \tau_D \rangle$. The time constant τ_D in
 1413 eq. (2.179) differs from the characteristic time τ_e in the Fermi gas expression for electronic
 1414 conductivity in metals, which is directly proportional to σ_0 [45]:

$$1415 \quad \tau_e = \frac{m}{ne^2} \sigma_0, \quad (2.180)$$

1416 where n is the number density of charge carriers of effective mass m and charge e . The reason for
 1417 the difference is that τ_e is the average time of travel between scattering events (collisions with
 1418 ions, electrons or phonons or by umklapp), whereas τ_D is the residence time between
 1419 (effectively instantaneous) jumps between adjacent sites. Nor is τ_D equal to τ_e for dielectric
 1420 relaxation, although they are related by an expression to be derived later. As noted already the
 1421 relaxation time τ_D is a measure of the rate of decay of the polarization at constant displacement,
 1422 i.e. the decay of the electric field E at constant D [44], whereas the dielectric retardation time is a
 1423 measure of the decay rate of the polarization at constant E , i.e. of D at constant E .

1424 Equation (2.179) implies that ionic conductivity cannot exceed ca. 10^3 Sm^{-1} , since τ_D
 1425 cannot reasonably be less than a vibrational lifetime and ϵ_∞ is rarely greater than about 10. The
 1426 vibrational τ_v lifetime is conveniently defined by the condition for critical damping (§1.11),
 1427 $\omega_0 \tau_v = 1$, so that for a typical vibrational frequency of about $f \approx 10^{12} \text{ Hz} \Rightarrow \omega \approx 6 \times 10^{12} \text{ rad/s}$ the
 1428 value of τ_v is about $2 \times 10^{-13} \text{ s}$ and

$$1429 \quad \sigma_{0,\text{max}} \approx \frac{e_0 \epsilon_\infty}{\tau_v} \approx \frac{(8.854 \times 10^{-12} \text{ F/m})(10)}{2 \times 10^{-13} \text{ s}} \approx 400 \text{ S/m} \quad (2.181)$$

1430 that is comparable with the highest conductivity observed for ionic conductors.

1431 The properties of the four basic functions for conductivity relaxation are conveniently
 1432 illustrated using a circuit comprising three elements in series: (i) a capacitance $C_s = 10^{-6} \text{ F} = 1 \mu\text{F}$
 1433 ; (ii) a parallel combination of a resistance $R_1 = 10^8 \Omega$ and a capacitance $C_1 = 10^{-12} \text{ F} (1 \text{ pF})$ (iii)
 1434 another parallel combination of a resistance $R_2 = 10^6 \Omega$ and a capacitance $C_1 = 10^{-12} \text{ F} (1 \text{ pF})$.

1435 The two parallel $R_p - C_p$ elements could for example simulate crystal and inter-crystal
 1436 impedances in a polycrystalline samples and the series capacitance C_s could simulate electrode
 1437 polarization. As discussed below this circuit has been used by several groups and will be referred
 1438 to as the "ideal conductivity" circuit. A Matlab®/GNU Octave code for generating the
 1439 corresponding spectra for the real and imaginary components of the four basic complex
 1440 relaxation functions (§2.1.9), and the corresponding complex plane plots of the imaginary
 1441 component vs. the real component, is given in Appendix AA.

1442 We discuss next the controversial electric modulus function (a discussion of many of the
 1443 issues surrounding it is given in [1]). The electric modulus $M^* = M' + iM''$ appears to have been
 1444 first defined by McCrum, Read and Williams [32], but its use in analyzing conductivity
 1445 relaxation was first initiated and exploited by Macedo and coworkers [44]. The usefulness of M^*
 1446 is illustrated by the simplest case of a constant conductivity σ_0 and constant relative permittivity
 1447 ϵ_∞ (the reason for the subscripts will become clear when distribution functions are considered
 1448 later). For convenience we copy eq. (2.101) here:

$$1449 \quad M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (a) \quad (2.182)$$

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (b).$$

1450 Insertion of the relations $\epsilon'' = \sigma_0 / e_0 \omega$ and $\epsilon' = \epsilon_\infty$ then yields

$$1451 \quad M' = \frac{1}{\epsilon_\infty^D} \left(\frac{\omega^2 \tau_D^2}{1 + \omega^2 \tau_D^2} \right) \quad (2.183)$$

1452 and

$$1453 \quad M'' = \frac{1}{\epsilon_\infty^D} \left(\frac{\omega \tau_D}{1 + \omega^2 \tau_D^2} \right). \quad (2.184)$$

1455 Thus M'' exhibits the desired (symmetric) peak as a function of $\ln(\omega)$. The components of ρ^*
 1456 are related to those of M^* by

$$1457 \quad \rho' = \frac{M''}{e_0 \omega} = \frac{\tau_D}{e_0 \epsilon_\infty^D} \left(\frac{1}{1 + \omega^2 \tau_D^2} \right) = \left(\frac{\rho_0}{1 + \omega^2 \tau_D^2} \right) \quad (2.185)$$

1458 and

$$1459 \quad \rho'' = \frac{M'}{e_0 \omega} = \frac{\tau_D}{e_0 \epsilon_\infty^D} \left(\frac{\omega \tau_D}{1 + \omega^2 \tau_D^2} \right) = \rho_0 \left(\frac{\omega \tau_D}{1 + \omega^2 \tau_D^2} \right), \quad (2.186)$$

1460 where $\rho_0 = 1/\sigma_0 = \tau_D / e_0 \epsilon_\infty^D$. Note that M'' and ρ'' have identical frequency dependencies but
 1461 are weighted by $1/\epsilon_\infty$ and ρ_0 respectively. This difference in weighting factors can be exploited
 1462 to considerable advantage in the analysis of ac conductivity (§2.3.5.6-§2.3.5.8).

1463 For dielectric relaxation M^* and ϵ^* are almost equivalent because a Debye peak in ϵ''
 1464 also yields a Debye peak in M'' [44] [see eqs. (2.132) and (2.133)]. The derivation for a Debye
 1465 dielectric without any conductivity is given in Appendix 2.1. It might appear that a peak in M''
 1466 could be due to either a conductivity or dielectric process and that M^* could not distinguish

1467 between them. This is not necessarily so, however, because the average relaxation time $\langle \tau_D \rangle$ will
 1468 be calculable from the limiting low frequency conductivity [eq. (2.73)] if the process is a
 1469 conductivity relaxation. If the peak in M'' is due to dielectric relaxation the retardation time will
 1470 not correlate with σ_0 . The archetypal example of dielectric relaxation being correlated with σ_0
 1471 occurs in the alkali silicate glasses and it was this correlation that originally led to the inference
 1472 that the residual dielectric loss (after subtraction of $\sigma_0 / \epsilon_0 \omega$) is due to the same alkali migration
 1473 process that produces σ_0 [27-31]. This led Macedo and collaborators [44] to first use M^* in the
 1474 analysis of conductivity relaxation.

1475 Note also that for dielectric relaxation

$$1476 \lim_{\omega \rightarrow 0} M'_{\text{dielectric}}(\omega) = 1 / \epsilon_0 \quad (2.187)$$

1477 compared with $\lim_{\omega \rightarrow 0} M'_{\text{conductivity}}(\omega) = 0$ for conductivity relaxation. The low frequency
 1478 conductivity relaxation limit for M' is revealing conceptually because M' is a measure of the
 1479 restoring force in response to an electric field perturbation. The low frequency limit of this
 1480 restoring force is finite for dielectric relaxation because the charge storage ability remains
 1481 nonzero: $\lim_{\omega \rightarrow \infty} \epsilon'(\omega) = \epsilon_0$. For conductivity relaxation the dielectric loss becomes infinite as

1482 $\omega \rightarrow 0$ (dissipation completely overrides any storage capability) and the restoring force is “short
 1483 circuited”. This is precisely analogous to the mechanical modulus going to zero as the viscosity
 1484 of a viscoelastic material dominates at low frequency and the elasticity disappears. The electric
 1485 modulus was first introduced to emphasize this mechanical analogy [32].

1486 An alternative to the electric modulus for analyzing materials in which the dielectric loss
 1487 and conductivity are correlated has been proposed by Johari [46]. This proposal is similar in style
 1488 to a mechanism for ionic conductivity proposed by Hodge and Angell [47] that was based on the
 1489 one-dimensional Glarum diffusion model for dielectric relaxation [§1.12.6, Chapter One]. Recall
 1490 that the Glarum model comprises a relaxing dipole that can relax either independently with
 1491 retardation time τ_0 or by the arrival of a defect of some kind that relaxes it instantly. Hodge and
 1492 Angell suggested that the dipole is a trapped ion/vacancy pair (that is known to exhibit Debye
 1493 dielectric behavior) and that the defects are itinerant ions that contribute to σ_0 . The average
 1494 activation energy for oscillation of trapped ions and that for ion migration are presumed to be
 1495 similar (perhaps identical), thus accounting for the nearly temperature invariant distribution of
 1496 conductivity relaxation times. The Glarum function is mathematically similar to the Davidson-
 1497 Cole function that has a Debye-like low frequency loss that is rarely observed. This low
 1498 frequency behavior arises from the Glarum assumption that the dipole has just one retardation
 1499 time. However if a distribution of dipole retardation times is assumed, corresponding to a
 1500 distribution of sites in an amorphous material for example, better agreement with experiment is
 1501 obtained without changing the essential physics of the Glarum model.

1502

1503 2.4.2 Distribution of Conductivity Relaxation Times

1504 Both M^* and ρ^* can be described in terms of a distribution of conductivity relaxation
 1505 times:

$$1506 \quad M^*(i\omega) = M_\infty \int_{-\infty}^{+\infty} g(\ln \tau_D) \left(\frac{i\omega\tau_E}{1 + \omega^2\tau_D^2} \right) d \ln \tau_D \quad (2.188)$$

1507 and similarly for $\rho^*(i\omega)$. A distribution of conductivity relaxation times affects the dispersion
1508 of the corresponding complex admittance functions $\varepsilon^*(i\omega)$ and $\sigma^*(i\omega)$:

$$1509 \quad \sigma_0 = \frac{e_0 \varepsilon_\infty^D}{\langle \tau_D \rangle} = \frac{e_0}{M_\infty^D \langle \tau_D \rangle}, \quad (2.189)$$

$$1510 \quad \sigma_\infty = e_0 \varepsilon_\infty^D \left\langle \frac{1}{\tau_D} \right\rangle = \frac{e_0}{M_\infty^D} \left\langle \frac{1}{\tau_D} \right\rangle, \quad (2.190)$$

1511 and

$$1512 \quad \varepsilon_0^D = \varepsilon_\infty^D \frac{\langle \tau_D^2 \rangle}{\langle \tau_D \rangle^2} \geq \varepsilon_\infty^D. \quad (2.191)$$

1513 A distribution of conductivity relaxation times is not easily distinguishable from
1514 dielectric and conductivity relaxations occurring together in modulus spectroscopy [36,44]
1515 although the dielectric relaxation will not be observable if $\tau_E \gg \tau_D$ because σ_0 will then exceed
1516 the limiting high frequency dielectric conductivity given by eq. (2.131):

$$1517 \quad \frac{\sigma'(\omega\tau_D \rightarrow 0)}{\sigma'_\mu(\omega\tau_E \rightarrow \infty)} = \frac{\sigma_0}{\sigma_\mu(\infty)} = \frac{\varepsilon_\infty}{\langle \tau_D \rangle} \left(\frac{\langle \tau_E \rangle}{\varepsilon_0 - \varepsilon_\infty} \right) = \frac{\varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} \frac{\langle \tau_E \rangle}{\langle \tau_D \rangle} \gg 1. \quad (2.192)$$

1518 This phenomenon has been directly observed in systems for which the dielectric retardation time
1519 is essentially constant but whose conductivity is increased by addition of electrolyte [48, 49] (see
1520 §2.3.6.9 below). This problem is ameliorated if conductivities can be measured with very high
1521 precision [50].

1522

1523 2.4.3 Constant Phase Element Analysis

1524 It is sometimes useful to have a circuit element for which the phase angle is independent
1525 of ω ,

$$1526 \quad W^*(i\omega) = W(\omega) \exp\left(\pm \frac{i\alpha\pi}{2}\right), \quad (2.193)$$

1527 where $W(\omega)$ is any real function and $0 < \alpha \leq 1$ is real; the positive sign in the exponent
1528 corresponds to an admittance and the negative sign to an impedance. As noted in Chapter One
1529 and §2.4.3, however, eq. (2.193) can only be valid over a restricted frequency range since
1530 otherwise the underlying distribution of relaxation/retardation times cannot be normalized.
1531 Equation (2.193) is a generalization of the Warburg impedance for which $\alpha = 0.5$.

1532 Almond and West [51] suggested the addition of such a parallel constant phase element
1533 admittance W [eq (2.193)] to the ideal parallel $R_p C_p$ element, in order to better simulate the
1534 typical admittance of solid electrolytes. The electrical response functions for this circuit are:

1535 *Conductivity*

$$\begin{aligned}
1536 \quad \sigma_{AW}^*(i\omega) &= kA_{AW}^* = k \left\{ R^{-1} + i\omega C_p + W_0\omega^\alpha \left[\cos\left(\frac{\alpha\pi}{2}\right) + i\sin\left(\frac{\alpha\pi}{2}\right) \right] \right\} \\
&= k \left\{ \left[R^{-1} + W_0\omega^\alpha \cos\left(\frac{\alpha\pi}{2}\right) \right] + i \left[\omega C_p + W_0\omega^\alpha \sin\left(\frac{\alpha\pi}{2}\right) \right] \right\} \\
&= [\sigma_0 + W_0'\omega^\alpha] + i[e_0\varepsilon_\infty\omega + W_0''\omega^\alpha]
\end{aligned} \tag{2.194}$$

1537 where $k =$ geometric cell constant, $W_0' = kW_0 \cos(\alpha\pi/2)$, $W_0'' = kW_0 \sin(\alpha\pi/2)$.

1538

1539 *Relative Permittivity*

$$1540 \quad \varepsilon_{AW}^*(i\omega) = \frac{\sigma^*(i\omega)}{i\varepsilon_0\omega} = \left\{ \left[\varepsilon_\infty + \left(\frac{W_0''}{e_0}\right)\omega^{\alpha-1} \right] - i \left[\frac{\sigma_0}{e_0\omega} + \left(\frac{W_0'}{e_0}\right)\omega^{\alpha-1} \right] \right\} \tag{2.195}$$

1541

1542 *Electric Modulus*

$$\begin{aligned}
1543 \quad M_{AW}^*(i\omega) &= \frac{i\omega\varepsilon_0}{\sigma^*(i\omega)} = \frac{i\omega\varepsilon_0}{[\sigma_0 + W_0'\omega^\alpha] + i[e_0\varepsilon_\infty\omega + W_0''\omega^\alpha]} \\
&= \frac{\omega\varepsilon_0 \left[(e_0\varepsilon_\infty\omega + W_0''\omega^\alpha) + i(\sigma_0 + W_0'\omega^\alpha) \right]}{[\sigma_0 + W_0'\omega^\alpha]^2 + [e_0\varepsilon_\infty\omega + W_0''\omega^\alpha]^2} \times \left(\frac{\varepsilon_\infty/\sigma_0^2}{\varepsilon_\infty/\sigma_0^2} \right) \\
&= \left(\frac{1}{\varepsilon_\infty} \right) \frac{\omega\tau_D \left\{ \left[1 + \left(\frac{W_0''}{\sigma_0}\right)\omega^\alpha \right] + i \left[e_0\varepsilon_\infty\omega + \left(\frac{W_0'}{\sigma_0}\right)\omega^\alpha \right] \right\}}{\left[1 + \left(\frac{W_0''}{\sigma_0}\right)\omega^\alpha \right]^2 + \left[e_0\varepsilon_\infty\omega + \left(\frac{W_0'}{\sigma_0}\right)\omega^\alpha \right]^2}
\end{aligned} \tag{2.196}$$

1544 Equation (2.19) yields the published Almond-West form with the substitutions

1545 $x = \omega(W_0'/\sigma_0)^{1/\alpha} = [(\sigma_0' - \sigma_0)/\sigma_0]^{1/2}$ and $\omega\tau_D = \left[(\sigma_0/W_0')^{1/\alpha} (e_0\varepsilon_\infty/\sigma_0) \right] x = Qx$:

$$1546 \quad M_{AW}^*(i\omega) = \left(\frac{Qx}{\varepsilon_\infty} \right) \frac{\left\{ \left[Qx + \tan\left(\frac{\alpha\pi}{2}\right)x^\alpha \right] + i \left[1 + x^\alpha \right] \right\}}{\left[1 + x^\alpha \right]^2 + \left[Qx + \tan\left(\frac{\alpha\pi}{2}\right)x^\alpha \right]^2} \tag{2.197}$$

1547

1548 *Resistivity*

$$1549 \quad \rho_{AW}^*(i\omega) = \frac{1}{\sigma^*(i\omega)} = \frac{M^*(i\omega)}{i\varepsilon_0\omega} = \rho_0 \frac{(1+x^\alpha) - i \left[Qx + \tan\left(\frac{\alpha}{2}\right)x^\alpha \right]}{(1+x^\alpha)^2 + \left[Qx + \tan\left(\frac{\alpha}{2}\right)x^\alpha \right]^2} \tag{2.198}$$

1550

1551 2.4.4 Determination of σ_0

1552 Several methods are available for estimating σ_0 when electrode polarization and
 1553 intergranular impedances obscure the limiting low frequency conductivity plateau. An accurate
 1554 value for σ_0 is important because, in addition to the obvious need for reliable data, its
 1555 contribution to ε'' must be subtracted for permittivity analyses (the attendant difficulties have
 1556 been discussed by Ravaine and Souquet [52, 53]). Accurate values of σ_0 are also needed in
 1557 order to determine reliable activation energies for conductivity. For example if $\log(\sigma)$ measured
 1558 at constant measuring frequency ω_{meas} is plotted against $1/T$ in the usual Arrhenius fashion,
 1559 spurious changes in slope can result from both polarization and bulk relaxation effects. If ω_{meas}
 1560 lies in a region where polarization is significant then the measured conductivity will be less than
 1561 σ_0 by an amount that increases with increasing temperature, because of the shift to higher
 1562 frequencies of the polarization σ' spectrum (which has essentially the same effective activation
 1563 energy as the sample conductivity). A fictitiously low activation energy is then obtained at high
 1564 temperatures as ω_{meas} probes deeper into the polarization relaxation. A spuriously low activation
 1565 energy can also occur at low temperatures when ω_{meas} lies within the bulk relaxation frequency
 1566 range, where σ' is often observed to increase as ω^α ($\alpha < 1$). In this case the measured
 1567 conductivity will exceed σ_0 by an amount that decreases with increasing temperature and the
 1568 measured activation energy will be smaller than the true value by the factor $\alpha = d \ln \sigma' / d \ln \omega$:

$$1569 \quad E_{a,obs} = E_{a,true} (1 - \alpha). \quad (2.199)$$

1570 In cases where $\alpha \approx 1$, as occurs in some electronic semiconductors [48], the fixed frequency
 1571 conductivity is therefore almost independent of temperature in the bulk relaxation temperature
 1572 region.

1573

1574 2.4.4.1 Analyses in the Complex Resistivity Plane

1575 Ravaine and Souquet [52,53] used the complex resistivity plane for determining σ_0 of
 1576 alkali silicate glasses in the presence of electrode polarization by low frequency extrapolation to
 1577 the real axis. They fitted the high frequency spectrum (i.e. sample relaxation) to the Cole-Cole
 1578 [54] function (see §1.12.5) and extrapolated the Cole-Cole semicircle to the real axis. For severe
 1579 polarization Armstrong et al. [55-59] used a similar method based on extrapolation of the high
 1580 frequency polarization spike to the real axis. This method is restricted to high conductivities
 1581 whose relaxation frequency lies above the measuring frequency range. As noted earlier the spike
 1582 sometimes occurs at an angle to the real axis rather than the ideal right angle that has been
 1583 attributed to "surface roughness" at the electrode interface [55].

1584

1585 2.4.4.2 Modulus and Resistivity Spectra

1586 In cases where polarization and conductivity relaxations overlap significantly and no
 1587 plateau in σ' is observed, σ_0 can be estimated from eq. (2.179) if $\langle \tau_D \rangle$ and ε_∞ are known.

1588 These can often be determined with sufficient precision by fitting $M''(\omega)$ to an appropriate

1589 empirical function: only the bulk relaxation is included in the fitted function because of the
 1590 insensitivity of M'' to high capacitance effects such as polarization and intergranular impedances.
 1591 For this application the fit to M'' should be weighted by the lower frequency data because these
 1592 reflect the longer relaxation time components of the distribution that contribute more
 1593 significantly to $\langle\tau_D\rangle$. The maximum in ρ'' , ρ''_{\max} , can also be used to estimate σ_0 : if the full
 1594 width at half height of the peak in ρ'' is Δ decades, then σ_0 can be estimated to within about
 1595 $\pm 10\%$ from the empirical relation

$$1596 \quad \sigma_0 \approx \frac{1}{1.75 \Delta \rho''_{\max}}. \quad (2.200)$$

1597 If only the maximum in ρ'' at ω_{\max} is observable σ_0 can still be estimated from the value of ρ'
 1598 at ω_{\max} by assuming $\rho''(\ln \omega)$ to be symmetric:

$$1599 \quad \sigma_0 \approx \frac{1}{2\rho'(\omega_{\max})}. \quad (2.201)$$

1600

1601 2.4.4.3 Complex Admittance Plane

1602 One of the first applications of complex plane plots was to polycrystalline yttria-zirconia
 1603 electrolytes by Bauerle [60]. Bauerle gave an excellent discussion of equivalent circuits and their
 1604 corresponding complex admittance plane plots, but the only circuit used in their data analysis
 1605 was a series combination of two parallel $R_p C_p$ elements and a series resistance R_s . One of the
 1606 parallel $R_p C_p$ elements in this circuit represents the electrode interface: the capacitance of a
 1607 double layer (electrode polarization) in parallel with the resistance of an oxygen gas-oxide ion
 1608 charge transfer process. The second $R_p C_p$ element represents an intergranular boundary
 1609 ("constriction") impedance, and the pure resistance simulates the bulk crystal. The
 1610 experimentally observed complex admittance plane plots were in excellent agreement with the
 1611 equivalent circuit behavior. The zero frequency conductivity predicted from the complex plane
 1612 plot was also in excellent agreement with four terminal data, and the expected dependence of the
 1613 electrode impedance on oxygen partial pressure was observed. Despite these successes, some
 1614 disadvantages of the method should be pointed out. First, in assuming that the bulk crystal acts as
 1615 a pure resistance the analysis implicitly assumes that the measuring frequencies are well below
 1616 the conductivity relaxation frequency, that can only be confirmed retrospectively. Second,
 1617 although there are three relaxing elements (since the sample resistance must realistically have a
 1618 capacitance in parallel with it), the complex admittance plane exhibits only two arcs that reflect
 1619 the differences between the relaxing elements. If the observed relaxations overlap significantly,
 1620 an assumption must be made about the shapes of the two relaxations before extrapolations are
 1621 made, i.e. a functional form for the extrapolating function must be chosen. Bauerle's data were
 1622 well described by the Cole-Cole function but this would not be expected to occur in general.

1623

1624 2.4.5 Combined Conductivity and Dielectric Relaxation

1625 These two relaxation phenomena can occur together provided the conductivity relaxation
 1626 occurs at lower frequencies than any dielectric relaxation, otherwise the increase in ε'' as f
 1627 decreases will dominate any dielectric loss.

1628

1629 2.4.6 Examples

1630 2.4.6.1 Electrode Polarization and Bulk Relaxation in the Frequency Domain

1631 Consider an idealized equivalent circuit similar to that used by Bauerle in which the
 1632 series resistance is replaced by a series capacitance. Specific values of the parallel $R_p C_p$ elements
 1633 are $[R_1 = 10^8 \Omega, C_1 = 10^{-11} \text{F} \Rightarrow \tau_1 = R_1 C_1 = 10^{-3} \text{s}]$, $[R_2 = 10^6 \Omega, C_2 = 10^{-11} \text{F} \Rightarrow \tau_2 = R_2 C_2 = 10^{-5} \text{s}]$ and
 1634 $[C_s = 10^{-6} \text{F}]$ so that the distribution of conductivity relaxation times comprises two delta
 1635 functions at $\tau_1 = 10^{-3} \text{s}$ and $\tau_2 = 10^{-5} \text{s}$. The shorter relaxation time element simulates the crystal
 1636 impedance in a polycrystalline preparation, the longer relaxation time element simulates an
 1637 intergranular impedance, and the series capacitance simulates electrode polarization. This circuit
 1638 has been found to be qualitatively useful in describing the electric response of a variety of
 1639 conductors, including a superionic conductor [61], an electronic semiconductor [62], and a
 1640 normal ionic conductor [9]. The relaxation time averages are

$$1641 \quad \langle \tau_D^2 \rangle = \frac{\tau_1^2 + \tau_2^2}{2} = 5.0005 \times 10^{-9} \text{ s} \quad (2.202)$$

$$1642 \quad \langle \tau_D \rangle = \frac{\tau_1 + \tau_2}{2} = 5.05 \times 10^{-5} \text{ s} \quad (2.203)$$

$$1643 \quad \langle \tau_D^{-1} \rangle = \frac{\tau_1^{-1} + \tau_2^{-1}}{2} = 5.05 \times 10^{+5} \text{ s} \quad (2.204)$$

1644 The high frequency relative permittivity is (assuming $k = 1$ for convenience so that $C_0 = \epsilon_0$
 1645 numerically)

$$1646 \quad \epsilon_\infty = \frac{C_1 C_2}{\epsilon_0 (C_1 + C_2)} = 5.647 \quad (2.205)$$

1647 and the low frequency relative permittivity is

$$1648 \quad \epsilon_0 = \epsilon_\infty \frac{\langle \tau_D^2 \rangle}{\langle \tau_D \rangle^2} = (5.647) \frac{(5.005 \times 10^{-9})}{(5.05 \times 10^{-5})^2} = 11.083. \quad (2.206)$$

1649 The limiting low and high frequency conductivities are

$$1650 \quad \sigma_0 = \frac{\epsilon_0 \epsilon_\infty}{\langle \tau_D \rangle} = \frac{(8.854 \times 10^{-12})(5.647)}{(5.05 \times 10^{-5})} = 9.9 \times 10^{-7} \text{ S m}^{-1} \quad (2.207)$$

$$1651 \quad \sigma_\infty = \epsilon_0 \epsilon_\infty \langle 1/\tau_D \rangle = (8.854 \times 10^{-12})(5.647)(5.05 \times 10^{+5}) = 2.53 \times 10^{-5} \text{ S m}^{-1}. \quad (2.208)$$

1652

1653 (1) There are two peaks each in ρ'' and M'' spectra that reflect the different weighting of the
 1654 two functions – eqs. (2.184) and (2.186). The two ρ'' peak heights differ by the ratio of the
 1655 resistances $10^8 / 10^6 = 10^2$, whereas the M'' peaks are equal in height because the two
 1656 capacitances are equal. If the capacitances were different and the resistances the same then the
 1657 peaks in ρ'' would have the same height and those in M'' would differ. Also ρ'' increases
 1658 indefinitely at low frequencies due to C_s whereas M'' is unaffected.

1659 (2) After subtraction of the contribution of σ_0 to ϵ'' , and of the limiting high frequency

1660 contribution of ε_∞ to σ'' , both σ'' and ε'' exhibit a single peak at a frequency between the two
 1661 maxima exhibited in the M'' and ρ'' spectra. These single peaks in the admittance functions
 1662 occur because at intermediate frequencies the high frequency RC element behaves as a
 1663 resistance and the low frequency RC element behaves as a capacitance. As noted in §2.2.4 the
 1664 effectively series RC circuit will produce a single loss peak in the admittance, and this is a
 1665 disadvantage of admittance functions in analyzing series processes. For the electrode polarization
 1666 relaxation caused by C_s in series with the sample resistance $(R_1 + R_2)$ peaks in $\sigma'' - e_0 \varepsilon_\infty \omega$ and
 1667 $\varepsilon'' - \sigma_0 / e_0 \omega$ are observed at lower frequencies.

1668 (3) A low frequency decrease in σ' and increases in ε' and ρ'' are found that due to the
 1669 electrode polarization simulated by C_s . For expositional clarity the value of C_s was chosen to
 1670 ensure a clean separation between the simulated polarization and bulk relaxations but this does
 1671 not occur in typical experimental data.

1672 (4) The complex plane plots have both advantages and disadvantages compared with the
 1673 spectra. Two disadvantages are the inconvenience of locating the frequencies of maximum loss,
 1674 and of comparing these frequencies in M^* and ρ^* plots because of the opposite directions of
 1675 increasing frequency. On the other hand, complex plane plots are useful for extrapolations. For
 1676 example in highly conducting materials whose conductivity relaxation frequency $1/\langle\tau_D\rangle$ lies
 1677 above the measuring frequency, and for which electrode polarization is significant or even
 1678 severe, the polarization spike in the ρ^* plane can be extrapolated to the real axis to give an
 1679 estimate of $\sigma_0 = 1/\rho_0$. At frequencies above the conductivity relaxation frequency, σ_0 is
 1680 manifested as a spike in the ε^* plane, corresponding to the limiting values of
 1681 $\lim_{\omega \rightarrow 0} \varepsilon'' = \lim_{\omega \rightarrow 0} \sigma_0 / \varepsilon_0 \omega = \infty$ and $\lim_{\omega \rightarrow 0} \varepsilon' = \varepsilon_0$.

1682 *****

1683 1684 2.4.6.2 Conductivity Relaxation in Sodium β - Alumina

1685 The following permittivity, modulus and resistivity spectra of single crystal sodium β
 1686 -alumina at 113 K have been reported by Grant and Ingram [64,65]: (i) the ε'' spectrum
 1687 perpendicular to the conduction planes; (ii) the M'' spectra in orientations perpendicular and
 1688 parallel to the conducting planes; (iii) the Z'' spectrum in the parallel orientation. The frequency
 1689 of maximum Z'' in the parallel orientation was close to the frequency of maxima in M'' and ε''
 1690 measured in the perpendicular orientation, and the activation energy for the parallel resistivity
 1691 spectrum was close to that for the perpendicular dielectric loss spectrum. The data for the
 1692 perpendicular orientation were interpreted in terms of a Maxwell layered dielectric [65], with
 1693 each insulating spinel block being a capacitance and each conduction plane a resistance. The
 1694 activation energy for the dielectric loss was thus determined by that of the conductivity of the
 1695 conducting layers, that the data suggest is similar in directions parallel and perpendicular to the
 1696 conduction planes. The extraordinarily large width of the M'' spectrum for single crystal Na β -
 1697 alumina in the parallel orientation [66,67] indicates a very broad distribution of conductivity
 1698 relaxation times, and the resistivity and modulus spectra taken together suggested that the
 1699 distribution is bimodal. Grant and Ingram proposed that at 113 K the low frequency conductivity
 1700 is determined by an activated localized ion motion that is the same in both orientations. The

1701 higher frequency conductivity, which contributes to M'' but not to ρ'' , results from a relatively
 1702 free motion of ions crossing low energy barriers. These mechanisms are consistent with low
 1703 temperature localization of sodium ions deduced from NMR data [68]. Localized activation is
 1704 not the rate determining step at high temperatures and the well-established low activation energy
 1705 for conductivity in sodium β -alumina was observed. The spectra of M'' and Z'' for a
 1706 representative polycrystalline specimen at 113 K were also shown. The Z'' spectrum is
 1707 uninformative at this temperature, increasing steadily at low frequencies due to electrode
 1708 polarization. The M'' spectrum exhibited a maximum at about the same frequency as the single
 1709 crystal M'' spectrum observed perpendicular to the conduction planes, and a reproducible
 1710 shoulder was observed at about the same frequency as M'' observed parallel to the conduction
 1711 planes in single crystals.

1712 This work demonstrates that comparison of the functions M'' , ρ'' and ε'' can uncover
 1713 details of the conductivity behavior of sodium β -alumina that could not even be discussed if
 1714 only σ^* and ε^* data were used.

1715 1716 2.4.6.3 Complex Impedance Plane Analysis of Electrode Polarization in Sintered β - 1717 Alumina.

1718 The use of the complex impedance plane for extrapolating polarization phenomena to
 1719 obtain data on the bulk material was used extensively by Armstrong and coworkers in their
 1720 studies of superionic conductors such as Na β -alumina [55] and Ag-Rb iodide [54-58]. A spike
 1721 in the complex impedance plane corresponds to the low frequency increase in Z'' due to the
 1722 series electrode capacitance and extrapolation of this spike to the real axis yielded the limiting
 1723 low frequency value of Z' and therefore of ρ_0 . Different surface preparations were observed to
 1724 affect the overall impedance but all of the extrapolations gave the same values for ρ_0 . This
 1725 method is clearly most appropriate for very highly conducting materials whose conductivity
 1726 relaxation lies at frequencies well above those that are experimentally convenient.

1727 1728 2.4.6.4 Complex Impedance Plane Analysis of Atmosphere Dependent Electrode Effects in 1729 KHF_2

1730 Complex impedance plane analysis was also used by Bruinink and Broers [69] for the α
 1731 and β phases of KHF_2 . In an atmosphere of hydrogen with platinum paint electrodes, the
 1732 complex impedance plane plot of data for α - KHF_2 was consistent with a Warburg impedance in
 1733 parallel with the bulk resistance and capacitance [69], and extrapolation to the real axis gave a
 1734 value of ρ_0 in agreement with the separately determined four terminal dc value. This plot gave
 1735 no indication of interfacial polarization, consistent with α - KHF_2 being a proton conductor and
 1736 the platinum paint electrodes behaving as reversible hydrogen electrodes. This contrasted sharply
 1737 with the low frequency behavior of α - KHF_2 in a vacuum, where a double layer capacitance of
 1738 about 440 mF m⁻² per electrode in parallel with a Faradaic resistance of about $2 \times 10^4 \Omega\text{m}$ per
 1739 electrode produced an additional semicircle in the complex plane. For the polycrystalline β
 1740 -phase the complex plane plot was essentially unchanged for data taken in both a hydrogen
 1741 atmosphere and a vacuum [69] and is consistent with a Warburg impedance in series with a
 1742 parallel RC element, corresponding to electrode polarization due to blocking of K^+ and/or F^-

1743 charge carriers. An RC transmission line was used to rationalize the Warburg impedance in
1744 terms of bulk electrical relaxation.

1745

1746 2.4.6.5 Intergranular Effects in Polycrystalline Electrolytes

1747 The effects of intergranular material on the overall electrical response of polycrystalline
1748 electrolytes have been extensively documented. Only one example is discussed here [9,66]. The
1749 simplest equivalent circuit representation of such materials comprises two parallel RC elements
1750 in series, where one element is associated with a crystallite and the other with intergranular
1751 material. Armstrong et al. [70] have shown that such a series circuit can represent the principle
1752 features of polycrystalline electrolytes. Since the interface is thin and the permittivities of ionic
1753 solids typically vary by a factor of less than 10, the capacitance C_i associated with the interface is
1754 much higher than that of the grain C_p :

$$1755 \quad C_i = \frac{\epsilon_0 \epsilon' A_i}{d_i} \gg \epsilon_0 \epsilon' = k C_p \quad (2.209)$$

1756 where A_i is the average cross section area, d_i is the average thickness of the intergranular
1757 material, and $k = \epsilon_0 / C_0$ is the cell constant.

1758

1759 2.4.6.6 Intergranular Cracking

1760 Experimental M'' and ρ'' spectra for a polycrystalline material known to have
1761 intergranular cracking were shown in reference [9]. The spectra were similar to those for two
1762 parallel $R_p C_p$ elements in series although the experimental peaks were broader - they could be
1763 approximated as the sum of two Debye peaks of equal heights separated by about a decade in
1764 frequency, so that the maxima in Z'' and M'' could be approximated as $R_p / 4$ and $C_0 / 4 C_p$,
1765 respectively. Computed values of R and C for the intergranular and granular material in the
1766 cracked sample, using these approximations and assuming a resolution into symmetric ρ''
1767 peaks, are:

1768 *Lower Frequency (Intergranular) Relaxation in Cracked Sample*

$$1769 \quad \tau_i = \frac{1}{\omega_{\max(Z'')}} = 6.4 \times 10^{-6} \text{ s}, \quad (2.210)$$

$$1770 \quad R_i \approx 4Z''_{\max} = 6.4 \times 10^6 \Omega, \quad (2.211)$$

$$1771 \quad C_i = \frac{\tau_i}{R_i} \approx 1.0 \text{ pF}. \quad (2.212)$$

1772 *Higher frequency (Intragranular) Relaxation in Cracked Sample*

$$1773 \quad \tau_c = \frac{1}{\omega_{\max(Z'')}} = 1.6 \times 10^{-7} \text{ s}, \quad (2.213)$$

$$1774 \quad R_c \approx 4Z''_{\max} = 2.6 \times 10^6 \Omega, \quad (2.214)$$

$$1775 \quad C_c = \frac{\tau_c}{R_c} \approx 0.06 \text{ pF} \quad (2.215)$$

1776 The impedance spectrum was drastically altered after annealing out of the intergranular

1777 cracking [9] (Figure 2.14(C)). The remaining single peak in Z'' was essentially indistinguishable
 1778 from the high frequency peak in the cracked material, strongly suggesting that it was due to
 1779 intra-crystal relaxation and that the additional low frequency peak for the unannealed sample is
 1780 due to cracking and the consequent air gaps. Consistent with this, the modulus spectrum was
 1781 essentially unchanged by annealing since it is unaffected by the high capacitance cracks. These
 1782 estimates of the intragranular and intergranular resistances were confirmed by the σ_0 data: the
 1783 observed conductivity of the cracked sample was largely determined by the intergranular
 1784 resistance, and the ratio of the conductivities of the sample before and after annealing should
 1785 have been

$$1786 \frac{Z_{\max}^{\text{low}\omega} + Z_{\max}^{\text{high}\omega}}{Z_{\max}^{\text{high}\omega}} = \frac{2.25 \times 10^6}{0.65 \times 10^6} = 3.5, \quad (2.216)$$

1787 in fair agreement with

$$1788 \frac{\sigma_{\text{annealed}}}{\sigma_{\text{cracked}}} = 3.1. \quad (2.217)$$

1789 The combination of modulus and impedance spectroscopies once again revealed details that
 1790 could not be obtained from the original σ' and ε' data.

1791

1792 2.4.6.7 Intergranular Gas Adsorption

1793 The effects of oxygen and alkali doping on the electrical response of polycrystalline zinc
 1794 oxide were studied by Seitz and Sokoly [71]. Only the effects of oxygen pressure are discussed
 1795 here. An increase in conductivity was observed with decreasing oxygen pressure and the absence
 1796 of changes due to different electrode materials implied that adsorbed oxygen at grain surfaces
 1797 was responsible for the observed polarization of the sample. The conductivity and permittivity
 1798 were plotted explicitly as a function of frequency in this report and these data allowed M'' and
 1799 ρ'' spectra to be calculated without difficulty. The calculated M'' and ρ'' spectra exhibited two
 1800 partially resolved peaks whose estimated magnitudes are consistent with a thin (high
 1801 capacitance) high resistance layer determining the low frequency response. Both peaks in the M''
 1802 spectrum have comparable half widths (ca. 1.5 decades) and their relative maximum values
 1803 (8×10^{-4}) and (1.1×10^{-2}) are a good (inverse) measure of the relative capacitance of each
 1804 relaxation: $C_\ell / C_h \approx 13$. The resistance ratio R_ℓ / R_h of the low frequency high frequency
 1805 relaxation can then be estimated from the two values of f_{\max} (ca. 5×10^2 and 3×10^5 Hz) to be
 1806 about 45:

$$1807 \frac{R_\ell C_\ell}{R_h C_h} \approx 600 \approx \frac{13 R_\ell}{R_h} \Rightarrow \frac{R_\ell}{R_h} \approx 45. \quad (2.218)$$

1808 The conductivity estimated from the height of the lower frequency resistivity peak is 1.1×10^{-7}
 1809 S/m, in reasonable agreement with the low frequency plateau value of 1.3×10^{-7} S/m. From the
 1810 relative frequencies of the M'' maxima and the relative heights of the (partly resolved) ρ''
 1811 maxima, the conductivity of the high frequency relaxation is estimated to be about $10^{-6 \pm 1}$.
 1812 Because of its higher associated capacitance the lower frequency relaxation almost certainly
 1813 corresponds to an intergranular impedance, and its removal by a reduction in oxygen pressure
 1814 should therefore increase the sample conductivity by about 45 but have a small effect on the

1815 measured permittivity (since removal of a high series capacitance has little effect). This predicted
1816 change in resistivity agrees with the qualitative statement that conductivity increased with
1817 decreasing oxygen pressure [71].
1818

1819 Appendices

1820

1821 Appendix 2.1 – Derivation of M^* for a Debye Relaxation with No Additional Separate
1822 Conductivity

1823 These derivations are shown for pedagogical clarity rather than mathematical elegance.

1824 (1) $\Delta\varepsilon \equiv \varepsilon_0^E - \varepsilon_\infty^E; \tau_D = (\varepsilon_\infty^E / \varepsilon_0^E) \tau_E; M_0^E = 1 / \varepsilon_0^E; M_\infty^E = 1 / \varepsilon_\infty^E$

1825 (2) $M^* = 1 / \varepsilon^* \Rightarrow M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}; M'' = \frac{-\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$

1826 (3) $\varepsilon' = \varepsilon_\infty^E + \frac{(\varepsilon_0^E - \varepsilon_\infty^E)}{1 + \omega^2 \tau_E^2} = \varepsilon_\infty^E + \frac{\Delta\varepsilon}{1 + \omega^2 \tau_E^2}; \varepsilon'' = \frac{\Delta\varepsilon \omega \tau_E}{1 + \omega^2 \tau_E^2}$

1827
$$\begin{aligned} \varepsilon'^2 + \varepsilon''^2 &= (\varepsilon_\infty^E)^2 + \frac{2\varepsilon_\infty^E \Delta\varepsilon}{1 + \omega^2 \tau_E^2} + \frac{\Delta\varepsilon^2}{(1 + \omega^2 \tau_E^2)^2} + \frac{\Delta\varepsilon^2 \omega^2 \tau_E^2}{(1 + \omega^2 \tau_E^2)^2} \\ &= \frac{(\varepsilon_\infty^E)^2 (1 + \omega^2 \tau_E^2) + 2\varepsilon_\infty^E \Delta\varepsilon + \Delta\varepsilon^2}{1 + \omega^2 \tau_E^2} = \frac{(\varepsilon_0^E)^2 + (\varepsilon_\infty^E)^2 \omega^2 \tau_E^2}{1 + \omega^2 \tau_E^2} \end{aligned}$$

$$M' = \left(\frac{\varepsilon_\infty^E (1 + \omega^2 \tau_E^2) + \Delta\varepsilon}{1 + \omega^2 \tau_E^2} \right) \left(\frac{1 + \omega^2 \tau_E^2}{(\varepsilon_0^E)^2 + (\varepsilon_\infty^E)^2 \omega^2 \tau_E^2} \right) = \left(\frac{\varepsilon_0^E + \varepsilon_\infty^E \omega^2 \tau_E^2}{(\varepsilon_0^E)^2 + (\varepsilon_\infty^E)^2 \omega^2 \tau_E^2} \right) = \left[\frac{\varepsilon_0^E + \varepsilon_\infty^E \omega^2 \tau_E^2}{(\varepsilon_0^E)^2 \left(1 + \frac{(\varepsilon_\infty^E)^2}{(\varepsilon_0^E)^2} \omega^2 \tau_E^2 \right)} \right]$$

1828 (4)
$$= \frac{1}{\varepsilon_0^E} + \frac{\varepsilon_\infty^E \omega^2 \tau_E^2 - \frac{\varepsilon_\infty^2}{\varepsilon_0} \omega^2 \tau_E^2}{(\varepsilon_0^E)^2 \left(1 + \frac{(\varepsilon_\infty^E)^2}{(\varepsilon_0^E)^2} \omega^2 \tau_E^2 \right)} = \frac{1}{\varepsilon_0^E} + \frac{\frac{\varepsilon_\infty^E}{(\varepsilon_0^E)^2} \omega^2 \tau_E^2 - \frac{(\varepsilon_\infty^E)^2}{(\varepsilon_0^E)^3} \omega^2 \tau_E^2}{\left(1 + \frac{(\varepsilon_\infty^E)^2}{(\varepsilon_0^E)^2} \omega^2 \tau_E^2 \right)} = \frac{1}{\varepsilon_0^E} + \frac{\left(\frac{1}{\varepsilon_\infty^E} - \frac{1}{\varepsilon_0^E} \right) \frac{(\varepsilon_\infty^E)^2}{(\varepsilon_0^E)^2} \omega^2 \tau_E^2}{\left(1 + \frac{(\varepsilon_\infty^E)^2}{(\varepsilon_0^E)^2} \omega^2 \tau_E^2 \right)}$$

$$= \frac{1}{\varepsilon_0^E} + \frac{\left(\frac{1}{\varepsilon_\infty^E} - \frac{1}{\varepsilon_0^E} \right) \omega^2 \tau_D^2}{(1 + \omega^2 \tau_D^2)} = M_0^E + \frac{(M_\infty^E - M_0^E) \omega^2 \tau_D^2}{(1 + \omega^2 \tau_D^2)}$$

1829

$$M'' = \left(\frac{-\Delta\varepsilon\omega\tau_E^2}{1 + \omega^2\tau_E^2} \right) \left(\frac{1 + \omega\tau_E^2}{(\varepsilon_0^E)^2 + (\varepsilon_\infty^E)^2 \omega^2\tau_E^2} \right) = \left(\frac{-\Delta\varepsilon\omega\tau_E}{(\varepsilon_0^E)^2 \left(1 + \frac{(\varepsilon_\infty^E)^2}{(\varepsilon_0^E)^2} \omega^2\tau_E^2 \right)} \right)$$

1830 (5)

$$= \left(\frac{-\Delta\varepsilon \frac{1}{\varepsilon_0} \frac{\varepsilon_\infty^E}{\varepsilon_0} \omega\tau_E}{\left(1 + \frac{(\varepsilon_\infty^E)^2}{(\varepsilon_0^E)^2} \omega^2\tau_E^2 \right)} \right) = \frac{(M_\infty^E - M_0^E)\omega\tau_D}{(1 + \omega^2\tau_D^2)}$$

1831

1832

1833

1834

A Matlab®/Octave program for computing the components of M^* with added conductivity is given below in Appendix 2.2.

1835 Appendix 2.2 Matlab®/GNU Octave Codes

1836 Computation Code for a Debye Relaxation with Additional Separate Conductivity σ_0 .

1837 The algebraic derivation is excessively tedious and is replaced here by a
 1838 Matlab®/GNU Octave code that plots both components of the ε^* and M^* functions. The values
 1839 of the input parameters are entered by editing the m-file.

```

1840
1841 % FUNCTION DebyeCondM Computes and Plots M* for Debye E* plus constant conductivity
1842 function HD = DebyeCondM
1843 w = logspace(-6,+6,1200);
1844 Logw = log10(w);
1845 E00 = 8.854E-12; % Vacuum permittivity in F/m
1846 E0D = 20; % Low f dielectric relative permittivity
1847 EinfD = 10; % High f dielectric relative permittivity
1848 DelE = E0D - EinfD; % Dielectric dispersion range
1849 EinfE = 3; % High f conductivity relative permittivity
1850 TauD = 10^-4 % Dielectric relaxation time
1851 Sigma0 = 10^-15; % Conductivity in S/m
1852 Tausig = E00*EinfE/Sigma0 % Conductivity relaxation time
1853 E2sig = Sigma0./(E00*w); % Conductivity contribution to E2
1854 % CALCULATE E1 and E2
1855 wTauD = w*TauD;
1856 Num = 1./(1 + wTauD.^2);
1857 E1 = EinfD + DelE*Num; % Debye E1
1858 E2 = DelE*wTauD.*Num + E2sig; % Debye E2 + Conductivity E2
1859 Denom = E1.^2 + E2.^2;
1860 M1 = E1./Denom;
1861 M2 = E2./Denom;
1862 subplot (2,2,1);
1863 plot (Logw, E1);
1864 ylabel("E1");
1865 subplot (2,2,2);
1866 plot (Logw, E2);
1867 ylabel("E2");
1868 subplot (2,2,3);
1869 plot (Logw, M1);
1870 ylabel("M1");
1871 subplot (2,2,4);
1872 plot (Logw, M2);
1873 ylabel("M2");
1874
1875 return
1876

```

1877 Appendix 2.3 Derivation of Debye Dielectric Expression from Equivalent Circuit

1878 Impedance of $R_s + C_s$ is

$$1879 \quad Z_s = R_s + 1/i\omega C_s = (1 + i\omega R_s C_s) / i\omega C_s = (1 + i\omega \tau_s) / i\omega C_s \quad (C1)$$

1880 and its admittance is

$$1881 \quad A_s = 1/Z_s = i\omega C_s / (1 + i\omega \tau_s) \quad (C2)$$

1882 where $\tau_s \equiv R_s C_s$. The total admittance is

$$1883 \quad A^* = i\omega C_s / (1 + i\omega \tau_s) + G_p + 1/(i\omega C_p) \quad (C3)$$

1884 and the complex capacitance is

$$C^* = A^*/i\omega = C_p + C_s / (1 + i\omega \tau_s) + G_p / i\omega$$

$$= \frac{C_p (1 + i\omega \tau_s) + C_s}{1 + i\omega \tau_s} + \frac{G_p}{i\omega} = \frac{[C_p (1 + i\omega \tau_s) + C_s] (1 - i\omega \tau_s)}{1 + \omega^2 \tau_s^2} + \frac{G_p}{i\omega}$$

$$1885 \quad = \frac{[C_p (1 + \omega^2 \tau_s^2) + C_s (1 - i\omega \tau_s)]}{1 + \omega^2 \tau_s^2} - \frac{iG_p}{\omega} \quad (C4)$$

$$= \frac{[C_p (1 + \omega^2 \tau_s^2) + C_s]}{1 + \omega^2 \tau_s^2} - \frac{i\omega \tau_s C_s}{1 + \omega^2 \tau_s^2} - \frac{iG_p}{\omega}$$

1886 from which eqs. (2.153) and (2.154) obtain.

1887

1888 REFERENCES (Needs Updating)

- 1889 [1] I. M. Hodge, K. L. Ngai, C. T. Moynihan, *J. Non-Cryst. Solids* **351** 104 (2005)
- 1890 [2] G. W. Chantry, "*Long-wave Optics*", Academic (1984), ISBN 0-12-168101-7
- 1891 [3] N. F. Hill, W. E. Vaughan, A. H. Price, and M. Davies, "*Dielectric Properties and*
1892 *Molecular Behavior*", p. 112, Van Nostrand (1969)
- 1893 [4] L. Onsager, *J. Am. Chem. Soc.* **58** 1486 (1936)
- 1894 [5] J. G. Kirkwood, *J. Chem. Phys.* **7** 911 (1939)
- 1895 [6] H. Frohlich, "*Theory of Dielectrics*", 2nd Ed. Vol **2** 72-73 (1958)
- 1896 [7] R. D. Mountain, *Proc. NYAS* **371** 252 (1981)
- 1897 [8] E. Fatuzzo and P. R. Mason, *Proc. Phys. Soc.* **90** 741 (1967)
- 1898 [9] R. L. Fulton, *Mol. Phys.* **29** 405 (1975)
- 1899 [10] I. M. Hodge, M. D. Ingram and A. R. West, *J. Electroanal. Chem.* **74** 125 (1976)
- 1900 [11] R. D. Armstrong, W. P. Race and H. R. Thirsk, *Electrochim Acta.* **13** 215 (1968)
- 1901 [12] R. D. Armstrong and R. Mason, *J. Electroanal. Chem.* **41**, 231 (1973)
- 1902 [13] R. D. Armstrong, *J. Electroanal. Chem.* **52** 413 (1974)
- 1903 [14] E. Warburg, *Wied. Ann.* **67** 493 (1899)
- 1904 [15] E. Warburg, *Ann. Phys.* **6** 125 (1901)
- 1905 [16] R. D. Armstrong, *J. Electroanal. Chem.* **52** 413 (1974)
- 1906 [17] D. Miliotis and D. N. Voon, *J. Phys. Chem. Solids* **30** 1241 (1969)
- 1907 [18] J. M. Wimmer and N. M. Tallan, *J. Appl. Phys.* **37** 3728 (1966)
- 1908 [19] R. D. Armstrong and R. A. Burnham, *J. Electroanal. Chem.* **72** 257 (1976)
- 1909 [20] R. D. Armstrong and K. Taylor, *J. Electroanal. Chem.* **63** 9 (1975)
- 1910 [21] R. Richert, *Adv. Chem. Phys.* **156** 101 (2014)
- 1911 [22] E. Bauer, *Cah. Phys.* **20** 1 (1944)
- 1912 [23] J. M. Stevels, *Handbuch der Physik*, Vol XX 372 (1957)
- 1913 [24] S. Glasstone, K. J. Layler and H. Eyring, "*The Theory of Rate Processes*", McGraw-Hill,
1914 New York, (1941)
- 1915 [25] H. E. Taylor, *J. Soc. Glass Technol.* **43** 124 (1959)
- 1916 [26] R. J. Charles, *J. Appl. Phys.* **32** 1115 (1961)
- 1917 [27] J. O. Isard, *Proc. Inst. Elect. Engrs., Supplement No. 20* **109B**, 440 (1962)
- 1918 [28] J. O. Isard, *J. Non. Cryst. Solids* **4** 357 (1970)
- 1919 [29] G. Williams, D. C. Watt, S. B. Dev and A. M. North, *Trans. Faraday Soc.* **67** 1323
1920 (1971)
- 1921 [30] G. Williams and D. C. Watt, *Trans. Faraday Soc.* **66** 80 (1970)
- 1922 [31] P. Debye, "*Polar Molecules*", Chapter 1, Chemical Catalog Co., New York, (1929)
- 1923 [32] L. Hayler and M. Goldstein, *J. Chem. Phys.* **66** 4736 (1977)
- 1924 [33] N. G. Crum, B. E. Read, and G. Williams, "*Anelastic and Dielectric Effects in Polymeric*
1925 *Solids*", Dover, New York (1991)
- 1926 [34] K. W. Wagner, *Arch. Electrotech.* **2** 378 (1914)
- 1927 [35] R. W. Sillars, *J. Inst. Electr. Engrs* **80** 378 (1937)
- 1928 [36] L. K. H. van Beek, *Physica* **26** 66 (1960)
- 1929 [37] I. M. Hodge and C. A. Angell, *J. Chem. Phys.* **68** 1363 (1978)
- 1930 [38] J. B. Hasted and M. Shahadi, *Nature* **262** 777 (1976)
- 1931 [39] I. M. Hodge and C. A. Angell, *J. Phys. Chem.* **82** 1761 (1978)
- 1932 [40] G. S. Darbari and S. Petrucci, *J. Phys. Chem.* **73** 921 (1969)

- 1933 [41] G. S. Darbari, M. R. Richelson and S. Petrucci, *J. Chem. Phys.* 53 859 (1970)
- 1934 [42] J. E. Enderby and G. W. Neilsen, in "*Water. A Comprehensive Treatise*", Vol 6", Ed. F. Franks Plenum, New York (1978)
- 1935
- 1936 [43] D. Bertolini, M. Casseteri and G. Salvetti, *J. Phys. Chem* 76 3285 (1982)
- 1937 [44] P. B. Macedo, C. T. Moynihan and R. Bose, *Phys. Chem. Glasses* 13 171 (1972)
- 1938 [45] C. Kittel, "*Introduction to Solid State Physics*", 7th Ed., Wiley, (1996)
- 1939 [46] G. P. Johari and K. Pathmanathan, *Phys. Chem. Glasses* 29 219 (1988)
- 1940 [47] I. M. Hodge and C. A. Angell, *J. Chem. Phys.* 67 1647 (1977)
- 1941 [48] F. S. Howell, *Ph.D. Thesis*, Catholic University of America (1972)
- 1942 [49] I. M. Hodge and C. A. Angell, *J. Phys. Chem.* 82 1761 (1978)
- 1943 [50] H. P. Schwan, G. Schwarz, J. Maczrak and H. Pauly, *J. Phys. Chem.* 66, 2626 (1962)
- 1944 [51] D. P. Almond & A. R. West, *J. Non-Cryst. Solids* 88 222 (1986)
- 1945 [52] D. Ravaine and J.-L. Souquet, *J. Chim. Phys.* 71 693 (1974)
- 1946 [53] D. Ravaine, J. P. Diard and J. -L. Souquet, *Faraday Trans. II*, 1935 (1975)
- 1947 [54]. K. S. Cole and R. H. Cole, *J. Chem. Phys.* 9 341 (1949)
- 1948 [55] R. D. Armstrong and R. A. Burnham, *J. Electroanal. Chem.* 72 257 (1976)
- 1949 [56] R. D. Armstrong and W. I. Archer, *ibid*, 87 221 (1978)
- 1950 [57] R. D. Armstrong, T. Dickinson and P. M. Willis, *J. Electroanal. Chem.* 48 47 (1973)
- 1951 [58] R. D. Armstrong, T. Dickinson and P. M. Willis, *J. Electroanal. Chem.* 54 281 (1975)
- 1952 [59] R. D. Armstrong and K. Taylor, *J. Electroanal. Chem.* 63 9 (1975)
- 1953 [60] J. E. Bauerle, *J. Phys. Chem. Solids* 30 2657 (1969)
- 1954 [61] R. J. Grant, M. D. Ingram and A. R. West, *Electrochim. Acta* 22 729 (1977)
- 1955 [62] M. Pollak and T. H. Geballe, *Phys. Rev.* 122 1742 (1961)
- 1956 [63] D. W. Davidson and R. H. Cole, *J. Chem. Phys.* 18 1417 (1951)
- 1957 [64] R. J. Grant and M. D. Ingram, *J. Electroanal. Chem.* 83 199 (1977)
- 1958 [65] R. J. Grant, M. D. Ingram and A. R. West, *J. Electroanal. Chem* 74 125 (1976)
- 1959 [66] I. M. Hodge, R. J. Grant, M. D. Ingram and A. R. West, *Nature* 266 42 (1977)
- 1960 [67] R. J. Grant, M. D. Ingram and A. R. West, *Electrochim. Acta* 22 729 (1977)
- 1961 [68] E. Lang and H. -D. Ludemann, *Angew Chem. Int. Eng.* 21 315 (1982)
- 1962 [69] J. Bruinink and G. H. J. Broers, *J. Phys. Chem. Solids* 33 1713 (1972)
- 1963 [70] R. D. Armstrong, T. Dickinson and P. M. Willis, *Electroanal. Chem & Interfac. Electrochem.* 53 389 (1974)
- 1964
- 1965 [71] M. A. Seitz and T. L. Sokoly, *J. Electrochem. Soc.* 121 163 (1974)
- 1966 [72] I. M. Hodge and A. Eisenberg, *Macromolecules* 11 283 (1978)
- 1967