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2 CHAPTER TWO: ELECTRICAL RELAXATION
3 12/13/2017
4 [DRAFT 12]

Contents

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63

64 Preliminaries
65   The examples used to illustrate different applications are not central to the purpose of this
66 book and are not recent. Some of the applications have been discussed in an unpublished but
67 widely circulated paper by the present author that is reproduced in Appendix A (original errors
68 have been corrected and the conversion to the phase convention used by everyone except
69 electrical engineers has been made.)
70
71 2.1   Nomenclature
72 Italicized lower case letters are used for physical variables, e.g. {*x, y, z, r*} for distances, *t* for
73 time, and *q* for charge; italicized upper case letters are used for specific values of variables and
74 field magnitudes, e.g. {*X, Y, Z, R*}, *T, Q*. Vectors are denoted by bold face upper case letters with
75 an arrow $\vec{\mathbf{V}}$ and tensors are denoted by bold face upper case $\mathbf{T}$.
76 There are two time constants for relaxation of polarization, one for relaxation at constant electric
77 field (i.e. dielectric relaxation of the displacement $\vec{\mathbf{D}}$) denoted by τ_E and one for relaxation at
78 constant displacement (i.e. conductivity relaxation of the electric field $\vec{\mathbf{E}}$) denoted by τ_D.
79 Amongst other things these two distinct time constants correspond to two microscopic time
80 constants for a single macroscopic dielectric time constant, as has been briefly discussed in ref.
81 [1].
82   Dielectric and conductivity relaxations can both occur in the same material over two
83 resolvable frequency ranges and the usual nomenclature for the low and high frequency limits of a
84 single relaxation process (e.g. ε_0 and ε_∞ for the relative permittivity) is ambiguous and has
85 caused confusion in a long standing debate about the legitimacy of the electric modulus
86 formalism. We introduce a new nomenclature here to distinguish the low and high frequency
87 limits for the two possible relaxations that, although somewhat clumsy, eliminates this confusion.
88 The two limits for a dielectric relaxation at constant $\vec{\mathbf{E}}$ are denoted by ε_0^E and ε_∞^E and the two
89 limits for a conductivity relaxation at constant $\vec{\mathbf{D}}$ are denoted by ε_0^D and ε_∞^D. Since a
90 conductivity relaxation must in general occur at lower frequencies than a dielectric relaxation for
91 the latter to be readily observed (with some exceptions depending on instrumental sensitivity)
92 then $\varepsilon_\infty^D = \varepsilon_0^E$, although overlap can occur.
93   Electric charge is denoted by *q* (Coulomb C), volume charge density by ρ $\left(\mathrm{C\,m^{-3}}\right)$,
94 surface charge density by σ $\mathrm{C\,m^{-2}}$, linear charge density by λ $\mathrm{C\,m^{-1}}$, current by *I* (Ampere = A =
95 $\mathrm{C\,s^{-1}}$), current density by *J* $\left(\mathrm{A\,m^{-2}}\right)$, electric potential by φ_E $\left(\mathrm{V=J\,C^{-1}}\right)$, electric field by *E*
96 $\left(\mathrm{N\,C^{-1}=V\,m^{-1}}\right)$, electric dipole moment by μ_E (C.m), resistance by *R* (Ohm = $\Omega = \mathrm{V\,A^{-1}}$), and
97 capacitance by C (Farad F = $\mathrm{C\,V^{-1}}$). The SI unit for conductance (=1/resistance) is the Siemen S
98 (equal to Ω^{-1}).
99

100   2.2   Electromagnetism
101   2.2.1   Units
102   Two systems of electromagnetic units are in use, the cgs (centimeter-gram-second) and the
103   MKS (meter-kilogram-second) or SI (Systeme Internationale). The SI system is the official
104   scientific system but the cgs system appears in older publications and since it is still used by
105   chemists and materials scientists its relationship to the SI system is delineated here. For
106   mechanics only the numerical value of physical quantities changes with the system of units, but in
107   electromagnetism there is an additional difference of approach: electric charge in the cgs system
108   is defined in the fundamental units mass-length-time whereas in the SI it is defined to be just as
109   fundamental as mass, length and time: this SI unit of charge is the Coulomb.
110   The cgs form of Coulomb's law for the force F between two point charges q_1 and q_2
111   separated by a distance r and immersed in a medium of (dimensionless) permittivity ε is
112

113
$$F = \frac{q_1 q_2}{\varepsilon r^2} \,, \qquad\qquad\qquad\qquad\qquad\qquad (2.1)$$

114

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

119
$$F = \frac{2\mu L I_1 I_2}{r} \,, \qquad\qquad\qquad\qquad\qquad\qquad (2.2)$$

120

121   that gives dimensions of $M^{1/2}L^{1/2}$ for the *electromagnetic unit* (emu) of charge. The esu and emu
122   units differ by a factor LT^{-1} that has the dimensions of speed and the value of the speed of light,
123   c. This is the reason that c enters into many cgs formulae. Numerically, $\text{emu} = c\,\text{esu}$ (c in cgs
124   units = 2.9979×10^{10} cm/s).
125   The Coulomb C is defined experimentally by its time derivative, the current in *amperes* A,
126   that in turn is determined using eq. (2.2). A constant μ_0 is inserted into the SI form for this
127   magnetic force to ensure consistency with the cgs system: the same force is produced by the same
128   currents separated by the same distance
129

130
$$F = \frac{\mu \mu_0 L I_1 I_2}{4\pi r} \,. \qquad\qquad\qquad\qquad\qquad\qquad (2.3)$$

131

132   Equations (2.2) and (2.3) reveal that $\mu_0 = 4\pi \times 10^{-7}\,\text{N.A}^{-2}$. The factor 4π arises from *Gauss's*
133   *Law* [eq. (1.150) and eq. (2.19) below]. The SI form of Coulomb's law is
134

135
$$F = \frac{q_1 q_2}{4\pi e_0 \varepsilon r^2} \,, \qquad\qquad\qquad\qquad\qquad\qquad (2.4)$$

136

137 where e_0 is a constant (the *permittivity* of free space), with dimensions $Q^2 M^{-1} L^{-3} T^2$ that
138 correspond to the units of capacitance per unit length (Farads meter^{-1}). Comparing eqs. (2.1) and
139 (2.4) reveals that
140
141 $$(esu)^2 = (Coulomb)^2 / 4\pi e_0.$$ (2.5)
142
143 The numerical relations between C, esu and emu are $C \approx 3 \times 10^9 \, esu \approx 10^{-1} emu$, where the
144 approximate equality arises from placing the speed of light at 3×10^8 m/s rather than
145 $2.9979... \times 10^8$ m/s. The dimensionless fine structure constant α in cgs units is
146 $\alpha = e^2 / hc = 2\pi e^2 / hc$ (*e* in esu) and in SI units is $\alpha = 2\pi e^2 / 4\pi e_0 hc = e^2 / 2 e_0 hc$ (*e* in
147 Coulomb). It is easily confirmed that the SI value of α is dimensionless and has the same
148 numerical value as the cgs value.
149   Having illustrated the cgs system to this point it is now dispensed with apart from one
150 exception: the unit for the molecular dipole moment. In the SI system this is the coulomb-meter
151 but this unit is inconveniently large and is rarely (ever?) used. The more common unit is the
152 *Debye,* defined as the dipole moment created by two opposite charges of 10^{-10} esu $\left(3.3 \times 10^{-20} \, C\right)$
153 separated by 1.0 Angstrom $\left(10^{-10} \, m\right)$. The persistence of this unit probably originates in the fact
154 that molecular dipole moments are of order unity when expressed in Debyes but of order 10^{-30} in
155 coulomb-meters. It is not clear to this author why a convenient SI unit such as 10^{-31} C.m ≈ 0.33
156 Debye or 10^{-30} C.m ≈ 3.3 Debye has not been introduced, especially since the SI unit nm has
157 replaced the Angstrom in optical spectroscopy.
158
159 2.2.2   Electromagnetic Quantities
160   Many of these are conveniently defined using a parallel plate capacitor comprising two
161 conducting flat plates, each of area *A* and separated by a distance *d*. The geometric "cell constant"
162 *k* is
163
164 $$k \equiv d / A.$$ (2.6)
165
166 Each plate has a charge of magnitude q_0 but of opposite sign (uniformly distributed since the
167 plates are conducting) that produces an electric potential difference V between the plates. The
168 capacitance is $C \equiv q_0 / V$ that has the units unit Farad = C V^{-1}. The surface charge density
169 $\sigma_0 = \pm q_0 / A$ on the plates induces an interfacial charge density $\mp\sigma_i$ on each surface of any
170 dielectric material between the plates. The *electric field* $\overset{\text{\textbar}}{\mathbf{E}}$, *polarization* $\overset{\text{\textbar}}{\mathbf{P}}$ and *displacement*
171 *vector* $\overset{\text{\textbar}}{\mathbf{D}}$ are perpendicular to the plates with magnitudes defined by the following table:
172

SI	*cgs*	
$D = \sigma_0$	$D = 4\pi \sigma_0$	(2.7)
$P = \sigma_i$	$P = \sigma_i$	(2.8)

176     $$\mathrm{e}_0 E = \sigma_0 - \sigma_i = D - P \qquad\qquad E = 4\pi\left(\sigma_0 - \sigma_i\right) = D - 4\pi P \qquad\qquad (2.9)$$

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     $$\overset{1}{\mathbf{D}} = \nabla\rho \qquad\qquad\qquad (2.10)$$

182

183   and

184

185     $$\overset{1}{\mathbf{E}} = \nabla\varphi_E . \qquad\qquad\qquad (2.11)$$

186

187   The inverse of eq. (2.11) is

188

189     $$\varphi_{1,2} = \int_{s_1}^{s_2} \overset{\mathbf{r}}{\mathbf{E}} g d \overset{\mathbf{r}}{\mathbf{s}} \qquad\qquad\qquad (2.12)$$

190

191   where $\varphi_{1,2}$ is the potential difference between the points s_1 and s_2. The *relative permittivity* ε

192   and *dielectric susceptibility* χ_d are defined in the following table:

193

194 | SI | cgs |
|---|---|

195 | $\varepsilon \equiv \dfrac{D}{\mathrm{e}_0 E}$ | $\varepsilon \equiv \dfrac{D}{E}$ | (2.13) |

196 | $\chi_d = \dfrac{P}{\mathrm{e}_0 E} = \dfrac{D - \mathrm{e}_0 E}{\mathrm{e}_0 E} = \varepsilon - 1$ | $\chi_d = \dfrac{P}{E} = \dfrac{D - E}{4\pi E} = \dfrac{1}{4\pi}\left(\varepsilon - 1\right)$ | (2.14) |

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

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

199   the unchanged charge density on the plates [eq. (2.9)]. The units of D and P (charge area^{-1})

200   correspond to dipole moment (charge-distance) per unit volume. In view of $\overset{1}{\mathbf{D}}$, $\overset{1}{\mathbf{E}}$ and $\overset{1}{\mathbf{P}}$ being

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

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

203   as scalars in this book.

204   The magnetic analogs of $D, E, P,$ $\mathrm{e}_0,$ ε and χ_d are, respectively, the magnetic induction

205     $B,$ the magnetic field $H,$ the magnetization $M,$ the permeability of free space, $\mu_0,$ the relative

206   permeability $\mu,$ and the magnetic susceptibility χ_m. The SI and cgs definitions are

207

208

209

SI	cgs	
$B = \mu_0 H$	$B = H$	(2.15)
$M = \dfrac{B}{\mu_0} - H$	$M = \dfrac{B - H}{4\pi}$	(2.16)
$\mu = \dfrac{B}{H}$	$\mu = \dfrac{B}{H}$	(2.17)
$\chi_M = \dfrac{M}{H} = \dfrac{B}{\mu_0 H} - 1$	$\chi_M = \dfrac{M}{H} = \dfrac{B}{4\pi H} - 1$	(2.18)

214

215   2.2.3   Electrostatics

216   Gauss's Law is

217

218

$$\oint_S e_0 \varepsilon \vec{\mathbf{E}} \cdot d\vec{\mathbf{A}} = q_{enclosed} \Rightarrow \oint_S \vec{\mathbf{D}} \cdot d\vec{\mathbf{A}} = q_{free},$$
(2.19)

219

220   where $q_{enclosed}$ is the total net charge within a closed surface S of magnitude A, ε is the relative

221   permittivity of the material enclosed by the surface, and the surface integral is the flux of the

222   electric field through the surface. For the definition in terms of $\overset{1}{\mathbf{D}}$ the quantity q_{free} does *not*

223   include the induced polarization charges because these are subsumed into the permittivity $e_0 \varepsilon$.

224   Equation (2.19) is the electrical version of the mathematical Gauss's Theorem in Chapter One [eq.

225   1.146)]. As noted in Chapter One the differential area vector $d\overset{1}{\mathbf{A}}$ of a surface is defined as having

226   a direction perpendicular to the plane of the surface, and for closed surfaces such as occur in

227   Gauss's Law the outward pointing direction is defined to be positive. The Gaussian surface is a

228   purely mathematical object that can be placed anywhere although it must have the same symmetry

229   as the system under study to be helpful. Thus information about charge distribution can be

230   inferred even though E is determined by the *total* enclosed charge.

231   Gauss's Law is now used to calculate $\overset{1}{\mathbf{E}}$ and the capacitance C for several geometries and

232   charge distributions. The geometrical objects and charges are taken to be immersed in a medium

233   of relative permittivity ε.

234

235   2.2.3.1 Point Charge (Coulomb's Law)

236   Define the Gaussian surface S as a sphere of radius r with a point charge q at its center. By

237   symmetry $\overset{1}{\mathbf{E}}$ is everywhere parallel to $d\overset{1}{\mathbf{a}}$ and has a constant magnitude E obtained from

238   $q = e_0 \varepsilon \oint \overset{1}{\mathbf{E}} \cdot d\overset{1}{\mathbf{A}} = 4\pi r^2 e_0 \varepsilon E$ so that

239

240

$$E = \frac{q}{4\pi \varepsilon e_0 r^2}.$$
(2.20)

241

242 2.2.3.2 Long Thin Rod with Uniform Linear Charge Density λ
243 　　　　Define the Gaussian surface to be a cylinder of radius r and length L, with the rod on its
244 central axis. Then $q = \varepsilon e_0 \oint_S \tilde{\mathbf{E}} \cdot d\mathbf{A} = \varepsilon e_0 E (2\pi r L)$ so that at a distance r from the axis

245

246 $$E = \frac{\lambda}{2\pi\varepsilon e_0 r} .$$ (2.21)

247
248 2.2.3.3 Flat Insulating Plate
249 　　　　Let a charge q be uniformly distributed over the two sides of a flat insulating plate of
250 "infinite area" (no edge effects) so that the charge on each surface is $q/2$. Define σ as the charge
251 per unit area so that the charge density on each surface is $\sigma/2$. Define the Gaussian surface as a
252 cylinder whose axis is parallel with the area vector of one side of the plate and has one end inside
253 the plate and the other end in a medium of relative permittivity ε. Then the electric field points
254 away from each surface of the plate (since q is positive) and $q/2 = \sigma A/2 = \varepsilon e_0 \oint_S \tilde{\mathbf{E}} \cdot d\mathbf{A} = \varepsilon e_0 E A$

255 so that
256

257 $$E = \frac{\sigma}{2e_0\varepsilon} .$$ (2.22)

258
259 This electric field is constant and independent of distance from the plate.

260
261 2.2.3.4 Flat Conducting Plate
262 　　　　Let the charge on each side of the plate be $q/2$ and define the Gaussian surface to be the
263 same as that for the insulating plate in §2.2.3.3. The electrostatic field inside a conductor is zero
264 so　that　the　electric　field　points　away　each　surface　of　the　plate　and
265 $q/2 = \sigma A/2 = e_0\varepsilon \oint_S \tilde{\mathbf{E}} \cdot d\mathbf{A} = e_0\varepsilon E A$ so that

266

267 $$E = \frac{\sigma}{2\varepsilon e_0} .$$ (2.23)

268
269 This electric field is again constant and is also independent of distance from the plate

270
271 2.2.3.5 Two Parallel Insulating Flat Plates
272 　　　　Consider charges $\pm q$ that are uniformly distributed over both surfaces of the plate. The
273 field between the plates is the vector sum of the fields from each plate. Since the field from the
274 positively charged plate points away from the positive plate and the field from the negatively
275 charged plate points toward the negative plate the two fields add up and the electric field is twice
276 that of eq. (2.22):
277

278    $$E = \frac{\sigma}{\varepsilon e_0}.$$ (2.24)

279

280   2.2.3.6 Two Parallel Conducting Flat Plates

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

285

286    $$E = \frac{\sigma}{\varepsilon e_0}.$$ (2.25)

287

288   The charge density on the outer surface of each plate is zero so that the electric field outside the
289   plates is also zero.

290   The capacitance is obtained from the voltage difference $V = E.d$ V between the plates and
291    $q = A\sigma_0$:

292

293    $$C = \frac{q}{V} = \frac{\sigma_0 A}{Ed} = \frac{\sigma_0 A/d}{e_0\varepsilon/\sigma_0} = (A/d)(e_0\varepsilon) = (e_0\varepsilon/k),$$ (2.26)

294

295   where k is the "cell constant" corresponding to the effective A/d for the container of the dielectric.

296

297   2.2.3.7 Concentric Conducting Cylinders

298   Define the inner and outer radii of two concentric conducting cylindrical plates to be a and
299   b, respectively, let their equal height be h, and let charges $+q$ and $-q$ be uniformly distributed on
300   the inside surfaces of each plate. Consider a concentric cylindrical Gaussian surface of radius
301    $a < r < b$ and height h, so that $q/e_0\varepsilon = \oint_S \mathbf{E} \cdot d\mathbf{A} = E(2\pi rh)$. Then

302

303    $$E = q/(2\pi rhe_0\varepsilon)$$ (2.27)

304

305   so that

306

307    $$V = \int_a^b Edr = \left(\frac{q}{2\pi he_0\varepsilon}\right)\int_a^b \frac{dr}{r} = \frac{q}{2\pi he_0\varepsilon}\ln\left(\frac{b}{a}\right)$$ (2.28)

308

309   and the capacitance is

310

311    $$C = \frac{q}{V} = \frac{2\pi he_0\varepsilon}{\ln\left(b/a\right)}$$ (2.29)

312
313 2.2.3.8 Concentric Conducting Spheres
314   Define the inner and outer radii of two concentric spherical conducting plates to be a and
315 b, respectively, and let charges $+q$ and $-q$ reside on the inside surfaces of each plate. Consider a
316 concentric spherical Gaussian surface of radius $a < r < b$ so that $q/e_0 = \oint_S \tilde{\mathbf{E}} \bullet d\mathbf{A} = E\left[4\pi r^2\right]$ and

317 $E = q/\left[4e_0\pi r^2\right]$. Then

318

319 $$V = \int_a^b E\,dr = \frac{q}{4\pi e_0 \varepsilon}\int_a^b \frac{dr}{r^2} = \frac{q}{4\pi e_0 \varepsilon}\left(\frac{1}{b}-\frac{1}{a}\right) = \frac{q}{4\pi e_0 \varepsilon}\left(\frac{a-b}{ab}\right)$$ (2.30)

320
321 and

322 $$C = \frac{q}{V} = 4\pi e_0 \varepsilon\left(\frac{ab}{b-a}\right).$$ (2.31)

323
324 2.2.3.9 Isolated Sphere
325   The capacitance of an isolated sphere is obtained from eq. (2.31) by taking the limit
326 $b \to \infty$ and for convenience placing $a = R$:
327
328 $$C = 4\pi e_0 \varepsilon R.$$ (2.32)

329
330 Thus larger spheres have larger capacitances.
331
332 2.2.4   Electrodynamics
333   Consider a constant voltage V applied across two parallel plates between which there is
334 now a conducting medium. Let the resistivity of the material be $\rho = R.k^{-1}$ (units ohm-meter) and
335 specific conductivity $\sigma = 1/\rho$ (units S m^{-1}), where R is the resistance between the plates in ohms
336 and the symbol S refers to the SI unit Siemen defined as the reciprocal of the ohm. The current
337 density $\mathbf{J}$ is the electric current per unit area (units A m^{-2}) so that $\mathbf{J}\rho = \mathbf{E}$. Unfortunately the
338 displacement current $dD/dt = d\sigma_0/dt$ (better named as the displacement current density) has no
339 symbol.
340   Electric current, symbol I, is defined as
341

342 $$I \equiv \frac{dq}{dt}$$ (2.33)

343
344 so that the total charge that passes across a plane through which a current I flows is
345

346 $$q = \int_0^t I\,dt'.$$ (2.34)

347

348   The electric potential φ_E is not defined for electrodynamics (see §2.5 below on Maxwell's
349   equations) and is replaced by the symbol voltage V (unfortunately also used for the unit volt).
350   Ohm's Law for the electrical resistance R (SI unit ohm (Ω) is then
351

352    $$R \equiv \frac{V}{I} \qquad (2.35)$$

353
354   and $\Omega = V/A$. An electrical conductor is said to be ohmic if, and only if, R is constant. This is
355   not the same as $dV/dI =$ constant: for example if $V = 1.0 + 2I$ so that $dV/dI = 2$ then
356    $R = 3\Omega$ for $I = 1\,\text{A}$, $R = 2.5\Omega$ for $I = 2\,\text{A}$, $R = 2.3\Omega$ for $I = 3\,\text{A}$.
357   Resistances dissipate power P given by $P = IV$ (recall that energy is given by QV and
358   power is the time derivative of energy). For ohmic resistances
359

$$P = IV$$
360    $$= I(IR) = I^2 R \qquad (2.36)$$
$$= (V/R)V = V^2/R.$$

361
362   2.2.5   Maxwell's Equations
363   These four equations summarize all that is known about electromagnetic phenomena –
364   they are essentially the electromagnetic equivalent of Newton's laws for mechanics but more
365   mathematically sophisticated because of the greater complexity of electromagnetic phenomena.
366   The differential forms of the four Maxwell equations are:
367

368    $$\vec{\nabla} \cdot \vec{D} = \rho \,; \qquad (2.37)$$
369    $$\vec{\nabla} \cdot \vec{B} = 0 \,; \qquad (2.38)$$
370    $$\vec{\nabla} \times \vec{E} = -\left(\frac{\partial \vec{B}}{\partial t}\right); \qquad (2.39)$$

371    $$\vec{\nabla} \times \vec{H} = \vec{J} + \left(\frac{\partial \vec{D}}{\partial t}\right) \qquad (2.40)$$

372    $$= \sigma \vec{E} + \left(\frac{\partial \vec{D}}{\partial t}\right) \qquad (2.41)$$

373    $$= \sigma \vec{E} + \text{e}_0 \left(\frac{\partial \varepsilon \vec{E}}{\partial t}\right). \qquad (2.42)$$

374
375   Equation (2.40) for a vacuum is equivalent to
376

377    $$\vec{\nabla} \times \vec{B} = \mu_0 \vec{J} + \mu_0 \text{e}_0 \left(\frac{\partial \vec{E}}{\partial t}\right), \qquad (2.43)$$

378 where σ is the specific electrical conductivity (units $\left(\Omega^{-1}\mathrm{m}^{-1}=\mathrm{Sm}^{-1}\right)$, $\overset{1}{\mathbf{B}}$ is the magnetic

379 induction, and $\overset{1}{\mathbf{H}}$ is the magnetic field. Equations (2.40) - (2.42) merit some discussion. The

380 equation $\overset{1}{\nabla}\times\overset{1}{\mathbf{H}}=\overset{1}{\mathbf{J}}$ might perhaps be expected instead of eq. (2.40) but this has the nonsensical

381 implication that there could never be any sources or sinks of current anywhere at any time,

382 because the vector identity $\overset{1}{\nabla}\mathrm{g}\!\left(\overset{1}{\nabla}\times\overset{1}{\mathbf{H}}\right)=0$ would then imply $\overset{1}{\nabla}\mathrm{g}\overset{1}{\mathbf{J}}=0$. The difficulty is resolved

383 by noting that for a charging or discharging parallel plate capacitor (for example) charge flow in

384 the external circuit joining the two capacitor plates, corresponding to dq_0/dt where q_0 is the

385 charge on the capacitor plates (see §2.1.2 above), must be compensated for by an opposite change

386 of the polarization charges between the plates (to ensure charge conservation). Thus

387

388 $$\overset{r}{\nabla}\mathrm{g}\!\left(\overset{r}{\nabla}\times\overset{r}{\mathbf{H}}\right)\equiv 0=\overset{r}{\nabla}\left[\left(\frac{\partial q_0}{\partial t}\right)-\left(\frac{\partial q_i}{\partial t}\right)\right] \qquad (2.44)$$

389 is ensured.

390 The term $\partial\overset{1}{\mathbf{D}}/\partial t$ in eq. (2.40) can correspond for example to a localized (molecular

391 diameter) effective spatial translation of charge due to rotation of an electric dipole about its

392 center of mass that has a close analogy to an ion hopping to an adjacent site (see §2.2.1.2). It is

393 called the *displacement current*. The term displacement "current" has been claimed to be a

394 misnomer but this is true only if a current is interpreted to be a long range translational migration

395 of charge. If the definition of current as dq/dt is adopted it is not a misnomer because q (on

396 capacitor plates for example) changes with time [eq. (2.44)], and furthermore a traditional current

397 must be present in an external circuit to compensate for $\partial q_i/\partial t$. Describing $\partial\overset{1}{\mathbf{D}}/\partial t$ as a

398 "fictitious current", as has been done in at least one popular text book, is disingenuous and

399 misleading because eq. (2.40) demonstrates that $\partial\overset{1}{\mathbf{D}}/\partial t$ is just as important in determining a

400 magnetic field as migration of individual charges.

401 The *vector potential* $\overset{1}{\mathbf{A}}$ is defined by

402

403 $$\overset{1}{\nabla}\times\overset{1}{\mathbf{A}}=\overset{1}{\mathbf{B}} \qquad (2.45)$$

404

405 and

406

407 $$\overset{r}{\mathbf{E}}=-\overset{r}{\nabla}\varphi_E-\frac{\partial\overset{1}{\mathbf{A}}}{\partial t}, \qquad (2.46)$$

408

409 and essentially ensures consistency between electrostatics and electrodynamics. Equation (2.45)

410 ensures eq. (2.38) because of the vector identity $\overset{r}{\nabla}\mathrm{g}\!\left(\overset{r}{\nabla}\times\overset{r}{\mathbf{A}}\right)=0$ and eqs. (2.45) and (2.46)

411 together ensure that eq. (2.39) remains true in dynamic situations where φ_E is undefined. The

412 vector potential is essentially an extension of the Coulomb potential φ_E to dynamic situations

413 because the definition of φ_E from $\overset{1}{\mathbf{E}}=\nabla\varphi_E$ [eq. (2.11)] is definable only in static situations, as the

414   following consideration indicates: if $\partial \dot{\mathbf{B}}/\partial t \neq 0$ then $\overset{\text{\tiny r}}{\nabla} \times \dot{\mathbf{E}} \neq 0$ by eq. (2.38) and the static
415   relation
416

417   $$\dot{\mathbf{E}} = \overset{\text{\tiny r}}{\nabla} \varphi_E \tag{2.47}$$

418

419   could then never hold because of the vector identity $\overset{\text{\tiny r}}{\nabla} \times \left(\overset{\text{\tiny r}}{\nabla} \varphi_E \right) = 0$. But $\dot{\mathbf{E}}$ is known to be

420   nonzero in dynamic situations [CHECK]. Similarly if $\dot{\mathbf{J}} \neq 0$ or $\partial \dot{\mathbf{D}}/\partial t \neq 0$ then there is no

421   potential φ_B for $\dot{\mathbf{B}}$ (defined by $\dot{\mathbf{B}} = \overset{\text{\tiny r}}{\nabla} \varphi_B$) because eq. (2.40) then implies $\overset{\text{\tiny r}}{\nabla} \times \dot{\mathbf{H}} = \overset{\text{\tiny r}}{\nabla} \times \dot{\mathbf{B}}/\mu\mu_0 \neq 0$

422   because of the same vector identity $\overset{\text{\tiny r}}{\nabla} \times \left(\overset{\text{\tiny r}}{\nabla} \varphi_B \right) = 0$. Both these difficulties are averted by the

423   introduction of $\dot{\mathbf{A}}$. Equation (2.46) is then consistent with eq. (2.39) since it guarantees
424

425   $$\overset{\text{\tiny r}}{\nabla} \times \overset{\text{\tiny r}}{\mathbf{E}} = \overset{\text{\tiny r}}{\nabla} \times \left(-\overset{\text{\tiny r}}{\nabla} \varphi_E - \frac{\partial \overset{\text{\tiny r}}{\mathbf{A}}}{\partial t} \right) = -\frac{\partial \overset{\text{\tiny r}}{\mathbf{B}}}{\partial t} \, . \tag{2.48}$$

426
427   Integral versions of Maxwell's equations include Faraday's Law:
428

429   $$\oint \overset{\text{\tiny r}}{\mathbf{E}} \cdot d\overset{\text{\tiny r}}{\mathbf{s}} = -\frac{d\Phi_B}{dt}; \qquad \Phi_B \equiv \int \overset{\text{\tiny r}}{\mathbf{B}} \cdot d\overset{\text{\tiny r}}{\mathbf{A}} = \text{magnetic flux} \tag{2.49}$$

430
431   and Ampere's law
432

433   $$\oint \overset{\text{\tiny r}}{\mathbf{B}} \cdot d\overset{\text{\tiny r}}{\mathbf{s}} = \mu_0 e_0 \frac{d\Phi_E}{dt} + \mu_0 I_{enclosed}; \qquad \Phi_E \equiv \oint \overset{\text{\tiny r}}{\mathbf{E}} \cdot d\overset{\text{\tiny r}}{\mathbf{A}} = \text{electric flux} \, . \tag{2.50}$$

434
435   Equation (2.42) provides a convenient demonstration of the equivalence of the complex
436   permittivity and complex conductivity. First convert eq. (2.42) from a vector equation to a
437   complex scalar equation:
438

439   $$\overset{\text{\tiny r}}{\nabla} \times \overset{\text{\tiny r}}{\mathbf{H}} = \sigma \overset{\text{\tiny r}}{\mathbf{E}} + e_0 \left(\frac{\partial \varepsilon \dot{\mathbf{E}}}{\partial t} \right) \Rightarrow \left| \overset{\text{\tiny r}}{\nabla} \times \overset{\text{\tiny r}}{\mathbf{H}} \right| = \sigma^* E^* + e_0 \varepsilon^* \left(\frac{\partial E^*}{\partial t} \right) . \tag{2.51}$$

440
441   For a sinusoidal excitation $E^* = E_0 \exp(-i\omega t)$ eq. (2.51) becomes
442

443   $$\begin{aligned}
\left| \overset{\text{\tiny r}}{\nabla} \times \dot{\mathbf{H}} \right| &= \sigma^* E_0 \exp(-i\omega t) - e_0 \varepsilon^* E_0 (i\omega) \exp(-i\omega t) \\
&= \left[\sigma^* - i\omega e_0 \varepsilon^* \right] E_0 \exp(-i\omega t) \\
&= \left[\varepsilon^* - \sigma^*/(i\omega e_0) \right] (-i e_0 \omega) E_0 \exp(-i\omega t),
\end{aligned} \tag{2.52}$$

444

445   indicating that both the complex conductivity $\left[\sigma*-i\omega e_0\varepsilon*\right]$ and complex permittivity

446     $\left[\varepsilon*-\sigma*/\left(i\omega e_0\right)\right]$ provide equivalent descriptions of electrical relaxation, as do the resistivity

447     $\rho*=1/\sigma*$ and electric modulus $M*=1/\varepsilon*$. All these different functions emphasize or suppress

448   different facets of experimental data in the same way that Fourier transforms do for example [see

449   eq. (2.106) below].

450

451   2.2.6   Electromagnetic Waves

452   The Maxwell equations together with the constitutive relations $\overset{\shortmid}{\mathbf{D}}=e_0\varepsilon\overset{\shortmid}{\mathbf{E}}$ and $\overset{\shortmid}{\mathbf{B}}=\mu_0\mu\overset{\shortmid}{\mathbf{H}}$

453   predict transverse electromagnetic (em) waves traveling at the speed of light c/n given by

454

455
$$\frac{c}{n}=\frac{\left(1/e_0\mu_0\right)^{1/2}}{\left(\varepsilon\mu\right)^{1/2}}=\frac{1}{\left(e_0\varepsilon\mu_0\mu\right)^{1/2}}\,,\tag{2.53}$$

456

457   where

458

459
$$n=\left(\varepsilon\mu\right)^{1/2}\tag{2.54}$$

460

461   is the refractive index. In a nonmagnetic material for which $\mu=1$ and $\varepsilon*=\left(n*\right)^2$

462

463
$$\left(n*\right)^2=\left(n'-in''\right)^2=\left(n'^2-n''^2\right)-2in'n''=\varepsilon*=\varepsilon'-i\varepsilon''\tag{2.55}$$

464

465   so that

466

467
$$\varepsilon'=n'^2-n''^2\tag{2.56}$$

468

469   and

470

471
$$\varepsilon''=2n'n''.\tag{2.57}$$

472

473   For the general case of a magnetic material where the relative magnetic permeability is also

474   complex, $\mu*=\mu'-i\mu''$,

475

476
$$\left(n*\right)^2=\left(n'^2-n''^2\right)-2in'n''=\left(\varepsilon'-i\varepsilon''\right)\left(\mu'-i\mu''\right)\tag{2.58}$$

477

478   so that

479

480
$$\left(n*\right)^2=\left(n'^2-n''^2\right)-2in'n''=\left(\varepsilon'-i\varepsilon''\right)\left(\mu'-i\mu''\right)=\left(\varepsilon'\mu'-\varepsilon''\mu''\right)-i\left(\varepsilon'\mu''+\varepsilon''\mu'\right),\tag{2.59}$$

481

482   and

483

484    $n'' = (\varepsilon'\mu'' + \varepsilon''\mu')$.   (2.60)

485

486   Thus absorption of electromagnetic energy by magnetically lossy materials is enhanced by a high
487   relative permittivity and dielectric loss is enhanced in magnetic materials.
488   The electric field component of a plane electromagnetic traveling wave of angular
489   frequency ω propagating in the $+x$ direction in a medium with refractive index n and speed c/n is

490    $E(x,t) = E_0 \exp\left\{-i\omega\left[t - \dfrac{nx}{c}\right]\right\}$,   (2.61)

491

492   and similarly for the magnetic field component. For complex $n^* = n' - in''$ eq. (2.61) becomes

493

494
$$E(x,t) = E_0 \exp\left\{-i\omega\left[t - \frac{(n'-n'')x}{c}\right]\right\}$$
$$= E_0 \exp\left\{-i\omega\left[t - \frac{n'x}{c}\right]\right\}\exp\left[\frac{-n''\omega x}{c}\right],$$
         (2.62)

495

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

498

499
$$I = E_0^2 \exp\left\{-2i\omega\left[t - \frac{(n'-in'')x}{c}\right]\right\}$$
$$= E_0 \exp\left\{-2i\omega\left[t - \frac{n'x}{c}\right]\right\}\exp\left[\frac{-2n''\omega x}{c}\right],$$
         (2.63)

500

501   that is to be compared with Beer's Law

502

503    $I = I_0 \exp(-\alpha x)$,   (2.64)

504

505   where α is the extinction coefficient (usually expressed in neper m^{-1} where the dimensionless
506   neper is used to emphasize that the logarithmic form of eq. (2.64) implies the Naperian
507   logarithm). Equations (2.63) and (2.64) yield

508

509    $\alpha(\omega) = \dfrac{2\omega n''(\omega)}{c}$.   (2.65)

510

511   The sign convention for imaginary numbers mentioned in the Introduction of Chapter One
512   is   seen   at   work   here.   If   the   sinusoidal   perturbation   was   defined   as

513 $E(x,t)=E_0 \exp\{+i\omega[t-nx/c]\}$ and the sign of the imaginary component of $\varepsilon*$ remained
514 negative then α would have to be negative and Beer's Law would predict unphysical exponential
515 growth through a medium. This can be resolved by making the imaginary component of $\varepsilon*$
516 positive but this corresponds to a dipole rotation that leads the excitation voltage rather than lags
517 it. Nonetheless this is the convention used by electrical engineers and is the price paid for the
518 "advantage" of having a positive sign in the complex exponential. An excellent account of phase
519 conventions is given in Chapter One of ref. [2].
520　　　　Insertion of eq. (2.57) into eq. (2.65) yields
521

522 $$\alpha(\omega)=\frac{\omega\varepsilon''(\omega)}{n'(\omega)c},\tag{2.66}$$

523
524 and since $\varepsilon''=\sigma'/(e_0\omega)$ then
525

526 $$\alpha(\omega)=\frac{\sigma'(\omega)}{n'(\omega)e_0 c}.\tag{2.67}$$

527
528 Thus n'',ε'',α and σ' are all measures of absorption of electrical energy:
529

530 $$\alpha=\frac{\sigma'}{ne_0 c}=\frac{\omega\varepsilon''}{nc}=\frac{2\omega n''}{c}.\tag{2.68}$$

531

532　　　　Ordinary em radiation comprises randomly distributed directions of polarization for the $\overset{\scriptscriptstyle 1}{\mathbf{E}}$
533 and $\overset{\scriptscriptstyle 1}{\mathbf{B}}$ fields (that are always perpendicular to one another). Radiation for which the direction of
534 polarization is constant and the same for all waves is said to be polarized. Reflected em waves are
535 partially polarized in the direction parallel to the reflecting surface, the extent of polarization
536 depending on the angle of incidence. Polaroid® sun glasses are polarized in the vertical direction
537 and therefore more strongly attenuate reflected waves. Reflected em waves are fully polarized at
538 the Brewster incident angle.
539
540 2.2.7　Local Electric Fields
541　　　　The electric field inside a dielectric medium is not equal to the applied field because of
542 electrostatic screening by the medium. This is a complicated problem that is well described in
543 Chapter One of ref. [3] (by N. E. Hill) and has been considered by Onsager [4], Kirkwood [5],
544 and Frohlich [6]. The complexity of the issue is illustrated by the Kirkwood relation between the
545 isolated molecular dipole moment μ_g observed in the gas phase and the relative permittivity ε_0^E
546

547 $$\frac{4\pi Ng\mu_g^2}{9k_B TVe_0}=\frac{\left(\varepsilon_0^E-\varepsilon_\infty^E\right)\left(2\varepsilon_0^E+\varepsilon_\infty^E\right)}{\varepsilon_0^E\left(\varepsilon_\infty^E+2\right)},\tag{2.69}$$

548

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

553

554 $$g = 1 + \sum_{i \neq j}^{N} \left\langle \cos\left(\theta_{ij}\right) \right\rangle, \tag{2.70}$$

555

556 where the averaged cosine $\left\langle \cos\left(\theta_{ij}\right) \right\rangle$ of the angle θ_{ij} between dipoles μ_i and μ_j can be
557 computed for specific orientation geometries.
558   The treatment of local field effects on the kinetics of dipole relaxation is even more
559 intricate because the reaction field produced by polarization of the dielectric medium by the
560 embedded dipole is in general out of phase with the applied field. These effects have been
561 discussed by Mountain [7]. A particularly important effect of local fields on relaxation
562 phenomenology is that a single macroscopic dielectric relaxation time corresponds to two
563 microscopic times. After a heated debate in the literature the accepted microscopic dipole
564 correlation function is the Fatuzzo and Mason [8] expression

565

566
$$\varphi(t) = \left(1 + \frac{\varepsilon_\infty}{2\varepsilon_0}\right)^{-1} \left[\exp\left(-\frac{t}{\tau_E}\right) + \left(\frac{\varepsilon_\infty}{2\varepsilon_0}\right) \exp\left(-\frac{\varepsilon_0}{\varepsilon_\infty}\frac{t}{\tau_E}\right) \right]$$
$$= \left(1 + \frac{\varepsilon_\infty}{2\varepsilon_0}\right)^{-1} \left[\exp\left(-\frac{t}{\tau_E}\right) + \left(\frac{\varepsilon_\infty}{2\varepsilon_0}\right) \exp\left(-\frac{t}{\tau_D}\right) \right], \tag{2.71}$$

567

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

573
574 2.2.8   Circuits
575   There are the four fundamental elements in analog passive circuits: resistance R;
576 capacitance C; self inductance L; mutual inductance M.

577
578 2.2.8.1 Simple Circuits
579 *Resistances in Series and in Parallel*
580   For resistances R_i connected in series the same current I must pass through each and the
581 sum of the voltages across each resistor equals the applied voltage. Thus $V = \sum V_i = I \sum R_i = IR_s$
582 and the equivalent series resistance R_s is

583

584     $R_s = \sum R_i$.   (2.72)

585

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

589

590     $1/R_p = \sum 1/R_i$.   (2.73)

591

592 *Capacitances in Series and in Parallel*
593   Capacitance C is defined as $C = q/V$, where V is the voltage across the capacitor and $\pm q$
594 are the charges on each of its ends. For capacitances C_i connected in parallel the same voltage
595 V must occur across each and the total charge q on each side of the equivalent parallel
596 capacitance C_p must equal the sum of charges q_i on each component. Thus
597 $q = \sum_i q_i = V \sum_i C_i = C_p V$ and the equivalent parallel capacitance C_p is given by

598

599     $C_p = \sum_i C_i$.   (2.74)

600

601   For capacitances connected in series the total voltage V across the series circuit equals the
602 sum of voltages across each capacitor. The magnitude of the charges q on each must be the same
603 (since no charge separation can occur across the short circuit joining them) so that
604 $V = q / C_s = \sum_i V_i = \sum_i q / C_i$ and the equivalent series capacitance C_s is given by

605

606     $\dfrac{1}{C_s} = \sum_i \dfrac{1}{C_i}$.   (2.75)

607

608 *Inductances in Series and in Parallel*
609   The self-inductance L is defined as $L \equiv V / (dI / dt)$ where V is the voltage across the
610 device and I is the current through it. Since V is in the numerator and I is in the denominator L is
611 an impedance akin to R. Impedances add in series so the equivalent series inductance L_s is

612

613     $L_s = \sum_i L_i$,   (2.76)

614

615 and since admittances add in parallel the equivalent parallel inductance I_p is
616

617     $\dfrac{1}{L_s} = \sum_i \dfrac{1}{L_i}$ (2.77)

618
619   For the sake of completion the mutual inductance M is now described although for reasons
620   given below it rarely comes into play for relaxation phenomena or insrumentation. It is defined as
621     $M = V_2 / (dI_1 / dt)$, where V_2 is the voltage induced on one side of the device by a time varying
622   current I_1 in the other. Rearrangement of this definition of M yields
623
624     $$V_2 = M\left(dI_1 / dt\right),$$ (2.78)
625
626   so that V_2 is smaller at lower frequencies when dI_1/dt is smaller. This is why transformer arm (ac
627   Wheatstone) bridges are useless at low frequencies. Series and parallel combinations of mutual
628   inductances add up in the same way as self inductances.
629
630   *Combined Series and Parallel Elements*
631   Consider two examples of a circuit in which an element Z_1 is in parallel with a series
632   combination of two elements Z_2 and Z_3. If these elements are resistances R_1, R_2 and R_3 then
633     $R_{23} = R_2 + R_3$ and
634

635     $$\frac{1}{R_{equiv}} = \frac{1}{R_1} + \frac{1}{R_2 + R_3} = \frac{R_1 + R_2 + R_3}{R_1\left(R_2 + R_3\right)}$$ (2.79)

636
637   or
638

639     $$R_{equiv} = \frac{R_1\left(R_2 + R_3\right)}{R_1 + R_2 + R_3}.$$ (2.80)

640
641   If these elements are capacitances C_1, C_2 and C_3 then
642     $1/C_{23} = 1/C_2 + 1/C_3 \Rightarrow C_{23} = C_2 C_3 /\left(C_2 + C_3\right)$ and
643

644     $$C_{equiv} = C_1 + C_{23} = C_1 + \frac{C_2 C_3}{C_2 + C_3} = \frac{C_1 C_2 + C_2 C_3 + C_3 C_1}{C_2 + C_3}.$$ (2.81)

645
646   2.2.8.2 AC Circuits
647   If a voltage $V(t) = V_0 \cos(\omega t) = \mathrm{Re}[V_0 \exp(-i\omega t)]$ is applied across a circuit the average
648   voltage over one period is zero but the ac power is not. Equation (2.36) indicates that power is
649   determined by the averages of I^2 and V^2 that are both proportional to the averages of $\sin^2(\omega t)$ or
650     $\cos^2(\omega t)$ over one cycle that are both equal to $\frac{1}{2}$. Thus
651

652     $$P_{average} = \left(V_0^2 / 2\right)R = I_0^2 R / 2.$$ (2.82)

653
654   The ac power dissipation is therefore given by the same relation for DC power dissipation if the

655   maximum ac voltage (V_0) and current (I_0) are replaced by $V_0/2^{1/2}$ and $I_0/2^{1/2}$ respectively. The
656   latter are referred to as rms (root mean square) voltages and currents. Electrical outlet ac voltages
657   such as 120V in North America are given as rms values; the peak voltage in North America is
658   therefore $(120\text{V})(2)^{1/2} = 170\text{V}$.

659   AC impedances $Z*(i\omega)$ are defined as $V*(i\omega)/I*(i\omega)$ and ac admittances $A*(i\omega)$ as
660    $I*(i\omega)/V*(i\omega)$. The imaginary components of $A*(i\omega)$ and $Z*(i\omega)$ are referred to as
661   reactances, and as shown below do not dissipate power.
662
663   *Resistances*
664   For a voltage $V = V_0 \exp(-i\omega t)$ applied across a resistance R the current is
665

666    $$I_R(i\omega t) = \frac{V(i\omega t)}{R} = \frac{V_0}{R}\exp(-i\omega t) = V_0 G\exp(-i\omega t) \tag{2.83}$$

667
668   so that the impedance is
669

670    $$Z_R^*(i\omega t) = \frac{V*(i\omega t)}{I*(i\omega t)} = \frac{V_0 \exp(-i\omega t)}{(V_0/R)\exp(-i\omega t)} = R \tag{2.84}$$

671
672   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
673   and independent of frequency.
674
675   *Capacitances*
676   For a capacitance C the current is
677

678    $$I_C(i\omega t) = \frac{dq(\omega t)}{dt} = C\frac{dV(i\omega t)}{dt} = V_0\left[-i\omega C\exp(-i\omega t)\right], \tag{2.85}$$

679
680   the capacitive impedance is
681

682    $$Z_C^*(i\omega t) = \frac{V*(i\omega t)}{I_C*(i\omega t)} = \frac{V_0 \exp(-i\omega t)}{V_0\left[-i\omega\exp(-i\omega t)\right]} = \frac{1}{-i\omega C} = \frac{i}{\omega C}, \tag{2.86}$$

683
684   the capacitive admittance is
685

686    $$A_C^*(i\omega t) = -i\omega C. \tag{2.87}$$

687

688 The capacitive admittance and admittance are therefore frequency dependent and imaginary.
689 Power dissipation per cycle in a capacitance is given by

690

$$
\begin{aligned}
P_C(t) &= \langle V_C(t) I_C(t) \rangle = \langle \left[V_0 \exp(-i\omega t) \right] V_0 \left[-i\omega C_p \exp(-i\omega t) \right] \rangle = -V_0^2 \omega C_p \langle \exp(-2i\omega t) \rangle \\
&= \langle -V_0^2 \omega C_p \left[\cos(-2\omega t) - i\sin(-2\omega t) \right] \rangle \\
&= \langle -V_0^2 \omega C_p \left[\cos(2\omega t) + i\sin(2\omega t) \right] \rangle \\
&= 0
\end{aligned}
\tag{2.88}
$$

692

693 because the averages of both $\cos(2\omega t)$ and $\sin(2\omega t)$ over one cycle are zero. The capacitive
694 impedance is therefore not a resistance if "resistance" is taken to imply power dissipation. This is
695 why an inductive or capacitive impedance is not considered to be an "ac resistance".

696

697 *Inductances*
698   For a self-inductance L the current is

699

700 $$
I_L(\omega t) = \int \left(\frac{V}{L} \right) dt = \int \left(\frac{V_0 \exp(-i\omega t)}{L} \right) dt = \left(\frac{V_0}{L} \right) \frac{\exp(-i\omega t)}{-i\omega}
\tag{2.89}
$$

701

702 so that inductive impedance is

703

704 $$
Z_L^*(i\omega t) = \frac{V^*(i\omega t)}{I_L^*(i\omega t)} = -i\omega L
\tag{2.90}
$$

705

706 and the inductive admittance is

707

708 $$
A_L^*(i\omega t) = \frac{1}{-i\omega L} = \frac{i}{\omega L} .
\tag{2.91}
$$

709

710 The inductive reactance is therefore also imaginary and frequency dependent. Power dissipation
711 in an inductance is given by

712

713 $$
\begin{aligned}
P_L(t) &= \langle V_L(t) I_L(t) \rangle = \langle \left[V_0 \exp(-i\omega t) \right] \left(\frac{V_0}{L} \right) \frac{\exp(-i\omega t)}{-i\omega} \rangle \\
&= -\frac{V_0^2}{-i\,\omega L} \langle \exp(-2i\omega t) \rangle = \frac{V_0^2}{i\,\omega L} \langle \exp(-2i\omega t) \rangle = 0.
\end{aligned}
\tag{2.92}
$$

714

715 Thus the power dissipated by a pure inductance is zero just like that of a capacitance ("pure"
716 meaning negligible resistance).

717
718 *Parallel Resistance and Capacitance*
719   Consider a voltage $V = V_0 \cos(\omega t)$ applied across a resistance R_p in parallel with a
720 capacitance C_p. The current I_R through the resistance is
721

722 $$I_R = \frac{V}{R_p} = \frac{V_0 \cos(\omega t)}{R_p} = V_0 \cos(\omega t) G_p = \text{Re}\left[V_0 G_p \exp(-i\omega t)\right] \qquad (2.93)$$

723
724 where $G_p = 1/R_p$ is the conductance. The current through the capacitance I_C is
725

726 $$\begin{aligned} I_C &= \frac{dq_C}{dt} = C_p \frac{dV}{dt} = -V_0 \omega C_p \sin(\omega t) \\ &= -V_0 \omega C_p \cos(\omega t - \pi/2) \text{Re}\left[-iV_0 \omega C_p \exp(-i\omega t)\right] \end{aligned} \qquad (2.94)$$

727
728 where q_C is the charge on the capacitor. Equation (2.94) implies that the sinusoidal (displacement)
729 current I_C lags the applied voltage by $\pi/2$ radians because $\sin(\omega t) = \cos(\omega t - \pi/2)$. The total
730 current through the parallel $R_p C_p$ circuit is
731

732 $$\begin{aligned} I = I_R + I_C &= V_0 G_p \cos(\omega t) - V_0 \omega C_p \sin(\omega t) \\ &= \text{Re}\left[V_0 G_p \exp(-i\omega t)\right] + \text{Re}\left[-iV_0 \omega C_p \exp(-i\omega t)\right] \\ &= \text{Re}\left\{V_0 \left[G_p - i\omega C_p\right] \exp(-i\omega t)\right\}. \end{aligned} \qquad (2.95)$$

733
734 The phase relations for the current are therefore conveniently expressed by defining the parallel
735 combination of resistance and capacitance as a complex admittance $A*$
736
737 $$A* = G_p - i\omega C_p, \qquad (2.96)$$
738
739 or as a complex impedance $Z*$
740

741 $$Z* = 1/A* = \frac{1}{G_p - i\omega C_p} = \frac{G_p}{G_p^2 + \omega^2 C_p^2} + \frac{i\omega C_p}{G_p^2 + \omega^2 C_p^2}. \qquad (2.97)$$

742
743 The complex capacitance is
744

745 $$C* = \frac{A*}{-i\omega} = C_p + \frac{iG_p}{\omega} \qquad (2.98)$$

746
747 and the complex electric modulus is
748

749     $M*(i\omega) = 1/C*(i\omega) = i\omega Z*(i\omega)$.   (2.99)

750
751   Equation (2.97) is equivalent to
752

753     $Z* = \dfrac{R_p}{1+\omega^2\tau_D^2} + \dfrac{iR_p\omega\tau_D}{1+\omega^2\tau_D^2}$ (2.100)

754
755 where
756
757     $\tau_D = R_p C_p$ (2.101)

758
759 is the Maxwell relaxation time (the reason for the subscript D is given below).
760   When normalized by the cell constant k (dimensions m^{-1}) the quantities $A*$, $Z*$ and $C*$ and
761 $M*$ become respectively the complex conductivity $\sigma* = kA*$, complex resistivity $\rho* = Z*/k$,
762 complex relative permittivity $\varepsilon* = kC*/e_0 = C*/C_0$ (where C_0 is the capacitance of the
763 measuring cell in a vacuum, usually equated to that in air), and complex modulus $M*$. Historically
764 the same symbol has been used for the complex electric modulus defined in terms of measured
765 circuit elements and as a material property, but this has not caused much (any?) confusion
766 probably because the inverse capacitance V/q has never been considered as a physically useful
767 quantity (in this respect it is not clear to this author why conductivity and resistivity should have
768 separate physical uses either).
769
770 *Series Resistance and Capacitance*
771   For a resistance R_s in series with a capacitance C_s
772

773     $Z*(i\omega) = R_s + \dfrac{1}{i\omega C_s} = R_s - \dfrac{i}{\omega C_s} = R_s\left(\dfrac{\omega\tau_E - i}{\omega\tau_E}\right)$,   (2.102)

774

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

776

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

778

779     $M*(i\omega) = i\omega Z*(i\omega) = i\omega\left(R_s - \dfrac{i}{\omega C_s}\right) = i\omega R_s\left(\dfrac{\omega\tau_E - i}{\omega\tau_E}\right) = \dfrac{R_s}{\tau_E}(1+i\omega\tau_E)$ (2.105)

780
781 where $\tau_E = R_s C_s$ that is generally not equal to $\tau_D = R_p C_p$.
782   The relations between the four response functions are conveniently summarized by [1,10]

783

$$\varepsilon*(i\omega) \quad \Leftrightarrow \quad 1/M*(i\omega)$$

784   c   c   . (2.106)

$$\sigma*(i\omega)/(ie_0\omega) \quad \Leftrightarrow \quad ie_0\omega/\rho*(i\omega)$$

785

786 2.2.8.3 Experimental Factors
787 *Cable Effects*
788   Cable impedances can be analyzed using transmission line methods that invoke an infinite
789 number of {L, C} components. One line of the cable is considered to be a series of inductances L
790 and the other line as a zero impedance wire, with capacitances C connecting the two between
791 every pair of inductances. In the limit of an infinite number of inductance and capacitance
792 elements the cable impedance $Z_{cable} = (L/C)^{1/2}$ is real and constant. Coaxial cables are made so
793 that C is 30 pF/ft and L is 0.075 μH/ft so that $Z_{cable} = (7.5 \times 10^{-8} H/3.0 \times 10^{-11})^{1/2} = 50\Omega$. Thus a
794 short cable with a 50 Ω resistor across it looks like an infinitely long cable and a 50 Ω load on the
795 cable has an ideal impedance match for maximum power transfer. Such a cable will also behave
796 as an inductor if short circuited so that for a high conductivity attached sample resonance effects
797 may be significant.
798

799 *Electrode Polarization*
800   This occurs for two and three terminal measurements when charge transfer does not occur
801 between an electrode and the sample material, i.e. when the applied voltage is less than the
802 decomposition potential of the sample (four terminal measurements are immune to this but they
803 do not produce reliable capacitance data and require separate sample preparation). In this case the
804 electrode-sample contact can be approximated as a capacitance C_s in series with the sample [11-
805 13] that is much larger than the sample capacitance C_p. If the amplitude of the applied potential is
806 too large (above the decomposition potential of the electrolyte) a Faradaic impedance [14, 15]
807 will also occur in parallel with this capacitance [16] that can sometimes be approximated as a
808 Warburg impedance (see §2.4.3).
809   A series capacitance does not affect $M''(\omega)$ and simply adds $1/C_s$ to $M'(\omega)$: the total
810 impedance $Z_{total}^*(i\omega)$ of the sample impedance $Z*(i\omega)$ and C_s is $Z_{total}^*(i\omega) = Z*(i\omega) + 1/i\omega C_s$
811 so that
812

813 $M*(i\omega) = i\omega Z_{total}^* = i\omega Z*(i\omega) + 1/C_s$.   (2.107)

814

815 It is a considerable advantage of the electric modulus function that $M''(\omega)$ is unaffected by
816 electrode polarization and other high capacitance phenomena. This is exploited in some of the
817 methods of data analysis discussed below but it should be noted that some researchers have
818 correctly noted that $M*$ also suppresses low frequency information (relative to $\varepsilon*$ for example),
819 but it can equally be claimed that $\varepsilon*$ suppresses high frequency information. The low frequency

820 high capacitance advantage of M^* is not shared by the imaginary component of the resistivity ρ''
821 because
822

823 $$\lim_{\omega \to 0} \rho''(\omega) \propto \lim_{\omega \to 0} \left(\frac{1}{k \, \omega C_s} \right) = \infty,$$ (2.108)

824
825 but the low frequency behavior of ρ' can be useful (see below).

826 Electrode polarization can however make the direct determination of the low frequency
827 quantities ε_0 and σ_0 difficult and sometimes impossible because it increases ε' above ε_0 at low
828 frequencies and, usually at lower frequencies, decreases σ' to below σ_0. Overlap between bulk
829 relaxations and these two electrode polarization effects prevents the observation of limiting low
830 frequency plateaus in $\varepsilon'(\omega)$ and/or $\sigma'(\omega)$. Although relaxation of electrode polarization often
831 occurs at much lower frequencies than the bulk relaxation,
832

833 $$\tau_{electrode} = \frac{\epsilon_0 C_s}{C_0 \sigma_0} >> \frac{\epsilon_0 C_p}{C_0 \sigma_0} = \tau_D,$$ (2.109)

834

835 the magnitude of the polarization dispersion can be very large [proportional to $(C_s - C_p) \approx C_s$]
836 and its high frequency tail can extend well into the bulk relaxation region. This phenomenon is
837 illustrated by the following representative average circuit quantities: a parallel capacitance
838 $C_p = 10 \, \text{pF}$ and parallel resistance $R_p = 10^7 \, \text{ohm}$ in series with a polarization capacitance of
839 $C_s = 10^4 \, \text{pF}$. Because both R_p and C_p will have distributions in a typical electrolyte there will be
840 dispersions in both ε' and σ' (see §2.4). The dispersion is centered around
841 $\omega \approx 1/(R_p C_p) = 10^4 \, \text{s}^{-1}$ and the low frequency plateau in ε' would normally then normally be
842 seen at ca. $\omega \approx 10^2 \, \text{s}^{-1}$, but this is dwarfed by the polarization capacitance at that frequency,
843 $C'_{pol}\left(\omega >> (R_p C_s)^{-1} \right) = C_s / (\omega^2 R_p^2 C_s^2) = 100 \, \text{pF}$, an order of magnitude higher than C_p. On the
844 other hand, the low frequency dispersion in conductivity due to polarization has barely begun at
845 $\omega = 10^2$: $\sigma_{ele} / \sigma_0 = \omega^2 \tau_{ele}^2 / (1 + \omega^2 \tau_{ele}^2) = 0.99$ for $\omega \tau_{ele} = \omega R_p C_s = (10^2)(10^{-1}) = 10$, where
846 the fact that the limiting high frequency conductivity for the Debye-like relaxation of electrode
847 polarization is σ_0:
848

849 $$\lim_{\omega \tau_{ele} \to \infty} \sigma'_{ele} = \frac{(\varepsilon_0 - \varepsilon_\infty)_{ele} \, \text{e}_0}{\tau_E} = \frac{(\varepsilon_0 - \varepsilon_\infty)_{ele} \, \text{e}_0 \varepsilon_\infty}{\tau_D \varepsilon_0} = \frac{(\varepsilon_0 - \varepsilon_\infty)_{ele} \, \sigma_0}{\varepsilon_0} \approx \sigma_0 \text{ for } \varepsilon_{0,ele} \, ? \, \varepsilon_{\infty,ele}$$ (2.110)

850
851 Effects similar to electrode polarization can arise from other causes, such as poor electrode
852 contact where a capacitance due to air gaps occurs in parallel with a resistance at the contact
853 areas. Poor contacts have been shown to give spurious dielectric losses in undoped alkali halides

854 [17], and is suspected to be responsible for the poor reproducibility of other dielectric data for
855 alkali halides [18]. Space charge effects can also produce a series capacitance at the electrode
856 [19,20].

857

858 2.3   Dielectric Relaxation
859   An excellent resource for dielectric relaxation is ref. [3], particularly Chapter One by N. E.
860 Hill. An excellent review of dielectric relaxation phenomena in supercooled and glassy materials
861 is given by Richert [21] that also includes references to modern measurement techniques.

862

863 2.3.1   Frequency Domain
864 2.3.1.1 Dipole Rotation
865   A freely rotating dipole in a sinusoidally varying electric field with an angular frequency
866 ω low enough that the dipole can keep up with the field behaves as a pure capacitance C_{pure}. The
867 current then lags the field by $\pi/2$ radians and the complex admittance is

868

869 $A* = i\omega C_{pure}$. (2.111)

870

871 If the dipole cannot keep up with the field because of friction with its environment it will lag by
872 an additional angle δ and a component of the current appears in phase with the voltage and is
873 measured as a resistance. Equation (2.94) is then replaced by

874

$$\begin{aligned} I_C &= -V_0\omega C_p \cos(\omega t - \pi/2 - \delta) \\ &= -V_0\omega C_p \left[\cos(\omega t - \pi/2)\cos\delta + \sin(\omega t - \pi/2)\sin\delta\right] \\ &= -V_0\omega C_p \left[\sin(\omega t)\cos\delta - \cos(\omega t)\sin\delta\right], \end{aligned}$$

875 (2.112)

876

877 and the term $+V_0\omega C_p \cos(\omega t)\sin\delta$ in eq. (2.112) is seen to be in phase with the applied voltage
878 $V = +V_0\cos(\omega t)$. This in phase component is of course zero when $\delta = 0$. Comparing eq. (2.112)
879 with eqs. (2.95) and (2.96) reveals that

880

881 $A* = \omega C_{pure}\sin\delta + i\omega C_{pure}\cos\delta$ (2.113)

882

883 and

884

885 $C* = C' - iC'' = C_{pure}\cos\delta - iC_{pure}\sin\delta$ (2.114)

886

887 so that

888

889 $G_p(\text{effective}) = \omega C_{pure}\sin\delta$ (2.115)

890

891 and

892
893     $C_p(\text{effective}) = C_{pure}\cos\delta$. (2.116)

894

895   At low frequencies when the lag angle δ tends to zero the effective capacitance equals C_{pure} and

896   G_p = 0, as must be. When normalized by the geometric capacitance associated with the cell

897   constant k, $C_0 = e_0/k$ where e_0 is the vacuum permittivity 8.854×10^{-12} F m^{-1}, the complex

898   capacitance becomes the complex permittivity, $\varepsilon^* = C^*/C_0$ so that

899
900     $\varepsilon^* = \varepsilon' - i\varepsilon''$ (2.117)

901
902   where

903

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

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

906
907   and

908

909     $\tan\delta = \dfrac{\varepsilon''}{\varepsilon'} = \dfrac{G_p}{\omega C_p}.$ (2.120)

910

911   Note that $\tan\delta$ is independent of the geometric capacitance C_0 and has the same frequency

912   dependence as ε'' but with a retardation time of $\left(\varepsilon_\infty^E / \varepsilon_0^E\right)^{1/2}\tau_E$ rather than τ_E. Equations (2.113)

913   and (2.114) imply

914
915     $A^* = i\omega C_0\varepsilon^*$ (2.121)

916
917   so that

918
919     $\sigma^* = kA^* = i\omega e_0\varepsilon^*$ (2.122)

920
921   and

922

923     $\rho^* = \dfrac{1}{\sigma^*} = \dfrac{1}{i\omega e_0\varepsilon^*}$ (2.123)

924
925   The complex electric modulus M^* is defined as the reciprocal of ε^*:

926

927 $M^* = 1/\varepsilon^*$ (2.124)

928

929 so that

930

931 $M^* = i\omega C_0 Z^* = i\omega e_0 \rho^*$. (2.125)

932

933 The functions σ^*, ε^*, ρ^* and M^* are all analytical and their components all conform to the

934 Cauchy-Riemann and Kronig-Kramers equations. The relationships between them are given in

935 eq. (2.106).

936 For a single relaxation time the (Debye) functions $\varepsilon^*(i\omega)$, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for

937 dielectric relaxation are

938

939 $\varepsilon^*(i\omega) = \varepsilon_\infty^E + \dfrac{\left(\varepsilon_0^E - \varepsilon_\infty^E\right)}{1 + i\omega\tau_E}$, (2.126)

940 $\varepsilon'(\omega) = \varepsilon_\infty^E + \dfrac{\left(\varepsilon_0^E - \varepsilon_\infty^E\right)}{1 + \omega^2\tau_E^2}$, (2.127)

941

942 and

943

944 $\varepsilon''(\omega) = \dfrac{\left(\varepsilon_0^E - \varepsilon_\infty^E\right)\omega\tau_E}{1 + \omega^2\tau_E^2}$, (2.128)

945

946 where ε_0^E and ε_∞^E are defined in §2.1.1 as the limiting low and high frequency limits of $\varepsilon'(\omega)$ at

947 constant electric field, respectively. Equations (2.127) and (2.128) yield a complex plane plot of

948 ε'' vs ε' that is a semicircle centered on the real axis at $\varepsilon' = \left(\varepsilon_0^E + \varepsilon_\infty^E\right)/2$. This is found by

949 eliminating $\omega\tau_E$ between equations (2.127) and (2.128) (see Appendix C in Chapter One for

950 details).

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

952 $\sigma'(\omega) = e_0\omega\varepsilon''(\omega) = \dfrac{e_0\left(\varepsilon_0^E - \varepsilon_\infty^E\right)\omega^2\tau_E}{1 + \omega^2\tau_E^2}$ (2.129)

953

954 and

955

956 $\sigma''(\omega) = e_0\omega\varepsilon_\infty^E + \dfrac{e_0\omega\left(\varepsilon_0^E - \varepsilon_\infty^E\right)}{1 + \omega^2\tau_E^2}$. (2.130)

957

958 Thus the real part of the conductivity of a Debye dielectric increases from zero at low frequencies
959 to a high frequency limit of
960

961 $$\sigma_{\infty} = \lim_{\omega \to \infty} \sigma'(\omega) = e_0 \left(\varepsilon_0^E - \varepsilon_{\infty}^E \right) / \tau_E ,$$ (2.131)

962

963 and the imaginary part diverges at high frequencies. Derivations of the Debye expressions for
964 $M'(\omega)$ and $M''(\omega)$ are instructive and straightforward but tedious – they are given in Appendix
965 2.1. The results are

966 $$M'(\omega) = M_0^E + \frac{\left(M_{\infty}^E - M_0^E \right) \omega^2 \tau_E^2}{1 + \omega^2 \tau_E^2}$$ (2.132)

967
968 and
969

970 $$M''(\omega) = \frac{\left(M_{\infty}^E - M_0^E \right) \omega \tau_E}{1 + \omega^2 \tau_E^2} ,$$ (2.133)

971
972 where $M_0^D = 1/\varepsilon_0^D$, $M_{\infty}^E = 1/\varepsilon_{\infty}^E$, and $\left(\varepsilon_{\infty}^E / \varepsilon_0^E \right) \tau_E = \tau_D$.

973 If a limiting low frequency conductivity σ_0 is present that is not physically related to the
974 dielectric loss process (e.g. ionic conductivity in a dilute aqueous solution), it must be subtracted
975 from the measured conductivity before the dielectric loss is calculated from eq. (2.128).
976 Otherwise the limiting low frequency dielectric loss $\lim_{\omega \to 0} \varepsilon'' \to 0$ will be masked by the rapid rise
977 from the conductivity contribution
978

979 $$\lim_{\omega \to 0} \varepsilon'' = \lim_{\omega \to 0} \frac{\sigma_0}{e_0 \omega} \to \infty .$$ (2.134)

980
981 It has been argued that this subtraction is physically meaningful only if the conductivity is
982 unrelated to the dielectric loss process (as in the aqueous solutions just mentioned). If the
983 dielectric loss peak correlates with σ_0 as occurs in alkali silicate glasses [22-28] and other
984 ionically conducting liquids and glasses then the subtraction of σ_0 can be regarded as artificial
985 and other methods of data analysis are preferred (although this position is not universally held).
986 This is the principle reason for not using the complex permittivity in analyzing highly conducting
987 materials and is the subject of §2.4.
988 If the decay function is nonexponential then dielectric relaxation can be described in terms
989 of a distribution of retardation times $g\left(\ln \tau_E \right)$ defined by the relations
990

991 $$\phi_E(t) = \int_{-\infty}^{+\infty} g\left(\ln \tau_E \right) \exp\left(-\frac{t}{\tau_E} \right) d \ln \tau_E$$ (2.135)

992
993   and
994

995
$$\int_{-\infty}^{+\infty} g\left(\ln \tau_E\right) d \ln \tau_E = 1,$$
(2.136)

996
997   so that eq. (2.126) generalizes to
998

999
$$\varepsilon^* - \varepsilon_\infty^E = \left(\varepsilon_0^E - \varepsilon_\infty^E\right) \int_{-\infty}^{+\infty} \frac{g\left(\ln \tau_E\right)}{1 + i\omega\tau_E} d \ln \tau_E.$$
(2.137)

1000
1001   The generalization of eqs. (2.127) and (2.128) are
1002

1003
$$\varepsilon'(\omega) = \varepsilon_\infty^E + \left(\varepsilon_0^E - \varepsilon_\infty^E\right)\left[\int_{-\infty}^{-} g\left(\ln \tau_E\right)\frac{1}{1+\omega^2\tau_E^2}\right] d \ln \tau_E = \varepsilon_\infty^E + \left(\varepsilon_0^E - \varepsilon_\infty^E\right)\left\langle \frac{\omega\tau_E}{1+\omega^2\tau_E^2}\right\rangle$$
(2.138)

1004
1005   and
1006

1007
$$\varepsilon''(\omega) = \left(\varepsilon_0^E - \varepsilon_\infty^E\right)\int_{-\infty}^{-} g\left(\ln \tau_E\right)\frac{\omega\tau_E}{1+\omega^2\tau_E^2} d \ln \tau_E = \left(\varepsilon_0^E - \varepsilon_\infty^E\right)\left\langle \frac{\omega\tau_E}{1+\omega^2\tau_E^2}\right\rangle.$$
(2.139)

1008
1009   The nth moments of a distribution function are
1010

1011
$$\left\langle \tau_E^n\right\rangle = \int_{-\infty}^{+\infty} \tau_E^n g\left(\ln \tau_E\right) d \ln \tau_E.$$
(2.140)

1012

1013   If the integral $\int_{-\infty}^{+\infty} g\left(\ln \tau_E\right) d \ln \tau_E$ diverges, as it does for a constant phase angle impedance for

1014   example, $g\left(\ln \tau_E\right)$ is not renormalizable and a constant phase angle impedance can therefore be

1015   valid only over a limited range in relaxation times. In terms of $\phi(t)$ the moments are
1016

1017
$$\left\langle \tau_E^n\right\rangle = \frac{1}{\Gamma(\omega)} \int_0^{+\infty} t^{n-1}\phi(t) dt$$
(2.141)

1018
1019   and
1020

1021 $$\left\langle \tau_E^{-n} \right\rangle = (-1)^n \left[\frac{d^n(\phi_E)}{dt^n} \right]_{t=0}$$ (2.142)

1022

1023 2.3.1.2 Ionic Hopping

1024   Chapter One of [3] by N. E. Hill discusses the studies of Frohlich [6] and others on the
1025 dielectric relaxation consequences of two state models. We select here the Frohlich account of an
1026 entity that has only two possible equilibrium positions 1 and 2. The entity could be a molecular
1027 dipole or an ion for example. If the transition probabilities between the two positions are w_{12} and
1028 w_{21} when there is no applied field then a Debye relaxation with a single relaxation time
1029 $\tau_E = 1/(w_{12} + w_{21})$ is   predicted   that   has   an   Arrhenius   temperature   dependence
1030 $\tau_E = A_E \exp(\Delta H / RT)$ where the pre-exponential factor A_E is a weak function of temperature and
1031 ΔH is the energy barrier that separates the two positions. As noted by Hill, however, a
1032 nonexponential decay function may result from local field effects.

1033

1034 2.3.2   Time Domain

1035   Consider the case where an electric field E is "instantaneously" increased from zero to E_0
1036 across a dielectric sample at time $t = t'$ and kept constant thereafter, i.e. $E(t) = E_0 h(t - t')$ where
1037 $h(t)$ is the Heaviside function (eq. (1.327)). The initially randomized dipoles will partially orient
1038 themselves over time and the polarization and displacement will both increase (the final average
1039 orientation will not be complete because of thermal fluctuations):

1040

1041 $$D(t) = D(0) + \left[D(\infty) - D(0) \right]\left[1 - \phi_E(t) \right],$$ (2.143)

1042

1043 where $D(0)$ and $D(\infty)$ are the limiting short time (high frequency) and long time (low
1044 frequency) values of $D(t)$ and $\phi_E(t)$ is the decay function for polarization at constant E
1045 corresponding to $D(t)$. The increase of D from zero to $D(\infty)$ is "instantaneous" compared with
1046 dielectric relaxation times (generally no shorter than about 10^{-11} s) and is due to polarization of
1047 molecular electron clouds that occurs roughly on optical time scales.
1048   It is sometimes convenient to approximate the relation between time domain data and
1049 $\varepsilon''(\omega)$ by the *Hamon approximation*

1050

1051 $$\varepsilon''(\omega) \approx \left(\varepsilon_0^E - \varepsilon_\infty^E \right)\left(\frac{-d\phi_E}{dt} \right)\left(\frac{5t}{\pi} \right),$$ (2.144)

1052

1053 obtained from the simplification that the normalized displacement current is given by

1054

1055 $$\left(\frac{-d\phi_E}{dt} \right) \sim t^{-n}.$$ (2.145)

1056

1057   No comparably simple relation exists between $\varepsilon'(\omega)$ and $\phi(t)$. Williams, Watt, Dev and North

1058   [29] have shown that for the Williams-Watt [30] decay function

1059

1060 $$\phi(t) = \exp\left[-\left(\frac{t}{\tau_0}\right)^{\beta}\right]$$ (2.146)

1061

1062   the Hamon approximation is accurate within 1% for $\omega\tau_0 > 1$ but fails for $\omega\tau_0 \leq 1$ and $\beta > 0.2$.

1063   Equation (2.144) therefore offers a high frequency approximation to the broadest frequency

1064   domain Williams-Watt functions that cannot be expressed in terms of named functions.

1065   The complex relative permittivity $\varepsilon^*(\omega)$ is related to the derivative of $\varepsilon(t)$ by

1066

1067 $$\varepsilon^*(i\omega) - \varepsilon_\infty^E = \left(\varepsilon_0^E - \varepsilon_\infty^E\right) \int_0^\infty -\left(\frac{d\phi_E}{dt}\right)\exp(-i\omega t)\,dt$$ (2.147)

1068

1069   where $\varepsilon_0^E = D(\infty)/E_0$ and $\varepsilon_\infty^E = D(0)/E_0$. In the simplest case $\phi_E(t)$ is exponential,

1070

1071 $$\phi_E(t) = \exp\left[-\left(\frac{t}{\tau_E}\right)\right],$$ (2.148)

1072

1073   and insertion of eq. (2.148) into eq. (2.147) yields the Debye equations (2.127) and (2.128)

1074   [Chapter One of ref. 3].

1075

1076   2.3.3   Temperature Domain

1077   In many situations ω and τ_E are approximately interchangeable variables. Since τ_E often

1078   varies strongly with temperature a narrow temperature range can be used as a surrogate for a wide

1079   frequency range. The temperature dependence of τ_E is often approximated by the Arrhenius

1080   relation

1081

1082 $$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right),$$ (2.149)

1083

1084   where τ_0 is independent of temperature, R is the ideal gas constant, and E_a is the activation

1085   energy. A better approximation is the Fulcher equation

1086

1087 $$\tau_E = A_F \exp\left(\frac{B_F}{T - T_0}\right)$$ (2.150)

1088

1089 where A_F, B_F and T_0 are positive constants. Thus the variables $\ln(\omega\tau)$ at constant ω, and E_a/RT
1090 or $B_F/(T-T_0)$, are equivalent for a single relaxation time dielectric. In this case eqs. (2.149) and
1091 (2.150) indicate that over the convenient temperature range from liquid nitrogen (77 K) to room
1092 temperature (300K) the retardation time can vary over a very large range. For example τ changes
1093 by a factor of 10^{25} for an average activation energy of 50 kJ/mol. The temperature variable is
1094 therefore extremely useful for scans of the total relaxation spectrum and is frequently used for
1095 polymers whose relaxation behavior is typically characterized by widely separated and broad
1096 relaxation processes. Activation energies E_a are obtained from plots of log frequency $\ln f$ against
1097 the inverse temperature $1/T_{\max}$ at which ε'' or $\tan\delta$ passes through its maximum:

1098

1099
$$\left\langle \frac{E_a}{R} \right\rangle = -\left[\frac{d\ln f}{d(1/T)} \right]. \tag{2.151}$$

1100

1101 It has been reported [32] that the activation energy obtained in this way is ambiguous because it
1102 depends on whether the derivative is determined in the isothermal frequency domain or in the
1103 temperature domain at constant frequency: the frequency domain plot of $\ln f_{\max}$ vs. $1/T$ was found
1104 to be strongly curved whereas the plot of $\ln f$ vs. $1/T_{\max}$ was found to be linear.
1105   Although temperature is useful because of its experimental convenience it is not
1106 quantitative because "everything changes with temperature". For example the dispersion
1107 $\left(\varepsilon_0^E - \varepsilon_\infty^E \right)$ can only be estimated because ε_0^E and to a less extent ε_∞^E are temperature dependent,
1108 although it can be estimated from the relation [33]
1109

1110
$$\left(\varepsilon_0^E - \varepsilon_\infty^E \right) \approx \left(\frac{2}{\pi R} \right) \left\langle \frac{1}{E_A} \right\rangle^{-1} \int_0^\infty \varepsilon''(T)\, d(1/T). \tag{2.152}$$

1111

1112 However eq. (2.152) is approximate because of two assumptions in its derivation that must be
1113 made for mathematical tractability: (i) $\left(\varepsilon_0^E - \varepsilon_\infty^E \right)$ is independent of temperature [32] and (ii)

1114 $\left\langle E_a \right\rangle = \left\langle 1/E_a \right\rangle^{-1}$ that is not generally true because of the Schmidt inequality (Chapter One)

1115

1116 $\left\langle E_A \right\rangle \left\langle 1/E_A \right\rangle^{-1} \geq 1$. $\tag{2.153}$

1117

1118 The approximation is clearly better for smaller temperature ranges. There are two situations where
1119 $\ln\omega$ and E_a/RT are not even approximately equivalent however: (i) functions for which ω and τ_E
1120 are not invariably multiplied together (for example the conductivity of a Debye dielectric, eq.
1121 (2.128)); (ii) distributions of retardation times that change with temperature.
1122

1123   2.3.4   Equivalent Circuits
1124   The electrical response for an exponential dielectric decay function, the Debye relations
1125   eqs. (2.127) and (2.128) plus any separate conductivity contribution σ_0, is simulated by an
1126   equivalent circuit comprising three parallel arms: a capacitance C_p, a series combination of R_s
1127   and C_s, and a resistance R_p. The relaxation part of the circuit is the series component $R_s + C_s$,
1128   the parallel resistance R_p corresponds to the separate conductivity, and the parallel capacitance
1129 C_p simulates the limiting high frequency permittivity. If for a particular range of frequencies the
1130   equivalent circuit of an experimental sample resembles $R_s + C_s$ and the frequency range
1131   encompasses $\omega = 1/(R_s C_s)$ then a dielectric loss peak will be observed in that frequency range. An
1132   example is electrode polarization in a conducting medium that at low frequencies is approximated
1133   by an electrode capacitance in series with the low frequency resistance of the sample. In this case
1134   a dielectric loss is observed with a retardation time given by the product of the polarization
1135   capacitance and sample resistance. Electrode polarization effects in solid electrolytes can often be
1136   a serious problem; they were briefly discussed in §2.2.8.3 and are discussed in detail in §2.3.6.1
1137   and §2.3.6.4 below.
1138   In terms of the equivalent circuit the components of the complex permittivity are (see
1139   Appendix 2.3)
1140

1141 $$\varepsilon'(\omega) = \frac{\sigma''}{e_0 \omega} = \left(\frac{1}{C_0}\right)\left(C_p + \frac{C_s}{1 + \omega^2 \tau_E^2}\right) \qquad (2.154)$$

1142
1143   and
1144

1145 $$\varepsilon''(\omega) = \frac{\sigma'}{e_0 \omega} = \left(\frac{C_s}{C_0}\right)\left(\frac{\omega \tau_E}{1 + \omega^2 \tau_E^2}\right) + \frac{\sigma_0}{e_0 \omega}, \qquad (2.155)$$

1146
1147   that reproduce the Debye relations eqs. (2.127) and (2.128). The low and high frequency limits of
1148 ε' are
1149

1150 $$\lim_{\omega \to 0} \varepsilon'(\omega) = \varepsilon_0 = \left(\frac{C_p + C_s}{C_0}\right) \qquad (2.156)$$

1151
1152   and
1153

1154 $$\lim_{\omega \to \infty} \varepsilon'(\omega) = \varepsilon_\infty = \left(\frac{C_p}{C_0}\right). \qquad (2.157)$$

1155

1156   Matlab®/GNUOctave codes for computing $M^*(i\omega)$ and $\rho^*(i\omega)$ with the added R_p are given in

1157   Appendix 2.2. A notable result is that $M*(i\omega)$ exhibits two relaxations corresponding to the

1158   Debye relaxation and an additional relaxation due to σ_0. The Debye relaxation for $M*(i\omega)$ is

1159   unaffected by R_p but the conductivity relaxation due to σ_0 is.

1160   As noted in §2.1 the occurrence of a dielectric and conductivity relaxation together raises

1161   an important nomenclature issue that has produced much confusion: the subscripts for denoting

1162   limiting low and high frequency limits can be ambiguous because these limits can refer to either

1163   the average dielectric relaxation frequency or to the average conductivity relaxation frequency. In

1164   particular, the quantity ε_∞ that enters into the expression for the conductivity relaxation time,

1165 $\langle\tau_D\rangle = e_0\varepsilon_\infty / \sigma_0$, is the *high* frequency limit for the *conductivity* relaxation, that may correspond

1166   to the *low* frequency limit for a separate dielectric relaxation. A proposed nomenclature to resolve

1167   this ambiguity was given above in §2.1 and has already been used in this section.

1168

1169   2.3.5   Interfacial Polarization

1170   In a homogeneous material $\nabla\cdot\mathbf{D} = e_0\varepsilon\nabla\cdot\mathbf{E} = 0$ implies $\nabla\cdot\mathbf{E} = 0$. At the interface between

1171   two dielectric materials of different permittivity, however, there is a discontinuity in ε and

1172 $\nabla\cdot\mathbf{D} = 0$ no longer implies $\nabla\cdot\mathbf{E} = 0$. The solution to this problem is obtained by applying

1173   Gauss's and Stokes' theorems to the interface with the result that the component of $\mathbf{E}$ tangential

1174   to the interface is continuous across the interface and the normal component of $\mathbf{D}$ is either

1175   continuous (no interfacial charge) or discontinuous if there is a free charge that is not the result of

1176   polarization of the materials on each side of the interface. These boundary conditions make

1177   macroscopic interfacial effects dependent on the geometry of the interface.

1178   Relaxation of interfacial polarization between alternating slabs of insulating dielectric and

1179   conducting layers, generically referred to as a *Maxwell Layered Dielectric*, is characterized by a

1180   single relaxation time τ_i given by

1181

1182 $$\tau_i = R_s C_s = \left(\frac{l_R}{l_C}\right)e_0\rho\varepsilon = \left(\frac{l_R}{l_C}\right)\left(\frac{e_0\varepsilon}{\sigma}\right)$$ (2.158)

1183

1184   where l_R is the thickness of the resistive layer with material resistivity ρ and l_C is the thickness

1185   of the capacitive layer with material permittivity ε.

1186

1187   2.3.6   Maxwell-Wagner Polarization

1188   Relaxation of interfacial polarization between a conducting sphere embedded in a

1189   dielectric continuum is known as *Maxwell-Wagner* (MW) *polarization*. Wagner [34] computed

1190   the loss tangent $(\tan\delta)$ for a volume fraction ϕ of spheres of material conductivity σ_1 and

1191   relative permittivity ε_1 suspended in a dielectric medium of relative permittivity ε_2, that was then

1192   generalized by Sillars [35] to suspensions of nonspherical particles. An excellent discussion of the

1193   phenomenon is given in ref [3] from which much of the following is distilled. We also draw from

1194   the paper by van Beek [36] who gave the Sillars formula and then considered the special case of

1195   suspended spheres, and noted that the often cited Wagner formula is only correct when the

1196 permittivities of the suspended material and the dielectric medium are equal and that the Sillars
1197 expression does not have this flaw.
1198   The Sillars expression for aspherical particles with aspect ratio a/b and a parallel to the
1199 field direction is
1200

1201 $$\tan \delta = \frac{\varepsilon_2 K}{\left[e_\infty \left(\varepsilon_2 K + e_\infty \right) \right]^{1/2}} \left(\frac{\omega \tau_0}{1 + \omega^2 \tau_0^2} \right),$$ (2.159)

1202
1203 with
1204

1205
$$K = \frac{n^2 \phi \varepsilon_2}{\left[(n-1)\varepsilon_2 + \varepsilon_1 \right]} \qquad (a),$$

$$e_\infty = \varepsilon_2 \left[1 + \frac{n\phi(\varepsilon_2 - \varepsilon_1)}{(n-1)\varepsilon_2 + \varepsilon_1} \right] \qquad (b),$$ (2.160)

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

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

1206
1207 where n is a function of the aspect ratio a/b. The limiting values for n are
1208

1209
$$n : 1 \qquad\qquad (a < b) \qquad (a)$$
$$n = 3 \qquad\qquad (a = b) \qquad (b) \qquad\qquad (2.161)$$
$$n \approx \left\{ \frac{a^2}{b^2 \left[\ln(2a/b) - 1 \right]} \right\} \qquad (a > b) \qquad (c),$$

1210
1211 Equation (2.161)(*c*) indicates that for needle-like particles oriented in the direction of the field the
1212 value of n can be large – for example $n \sim 50$ for $a = 10b$. Because $\tan \delta$ is roughly proportional to
1213 n^2 [eqs. (2.159) and (2.160)*a*] the Maxwell-Wagner-Sillars effect can produce very large
1214 dielectric losses. For spherical particles
1215

$$K = \frac{9\phi\varepsilon_2}{[2\varepsilon_2 + \varepsilon_1]} \qquad (a),$$

$$\mathrm{e}_\infty = \varepsilon_2 \left[1 + \frac{3\phi(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_2 + \varepsilon_1} \right] \qquad (b), \qquad\qquad (2.162)$$

$$T = \frac{\mathrm{e}_0[2\varepsilon_2 + \varepsilon_1]}{\sigma_1} \qquad (c),$$

and τ_0 is again given by eq. (2.160)d. The maximum value of $\tan\delta$ computed from eq. (2.159)d is therefore

$$\tan\delta_{\max} = \frac{\varepsilon_2 K}{2\left[\mathrm{e}_\infty\left(\varepsilon_2 K + \mathrm{e}_\infty\right)\right]^{1/2}} . \qquad\qquad (2.163)$$

This expression is inconveniently complicated but simplifies when $\phi \to 0$:

$$\lim_{\phi\to 0}\left(\tan\delta_{\max}\right) = \frac{9\phi\varepsilon_2}{2\left(2\varepsilon_2 + \varepsilon_1\right)} . \qquad\qquad (2.164)$$

The components of the complex relative permittivity for the Maxwell-Wagner phenomenon for this limiting case are conveniently expressed using three ancillary functions [36]:

$$\varepsilon_\phi = \varepsilon_2\left\{1 + \frac{3\phi(\varepsilon_1 - \varepsilon_2)}{2\varepsilon_2 + \varepsilon_1}\right\}, \qquad\qquad (2.165)$$

$$S = \frac{9\phi\varepsilon_2}{2\varepsilon_2 + \varepsilon_1}, \qquad\qquad (2.166)$$

$$T = \frac{\sigma_1}{\mathrm{e}_0\left(2\varepsilon_2 + \varepsilon_1\right)} . \qquad\qquad (2.167)$$

Then

$$\varepsilon'' = \frac{\left(\varepsilon_\phi S\omega T\right)}{1 + \omega^2 T^2} \qquad\qquad (2.168)$$

and

1241

1242 $$\varepsilon' = \varepsilon_\phi \left\{ 1 + \frac{S}{1 + \omega^2 T^2} \right\}.$$ (2.169)

1243

1244 The maximum in the observed dielectric loss $\varepsilon_{MW}^{"}$ is therefore

1245

1246 $$\varepsilon_{max}^{"} = \frac{9\phi\varepsilon_2^2}{2(2\varepsilon_2 + \varepsilon_1)} \left[1 + \frac{3\phi(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_{12} + \varepsilon_1} \right] \rightarrow \frac{9\phi\varepsilon_2^2}{2(2\varepsilon_2 + \varepsilon_1)},$$ (2.170)

1247

1248 that occurs at an angular frequency ω_{max} given by

1249

1250 $$\omega_{max} = 1/\tau_{MW} = \frac{\sigma_1}{e_0(2\varepsilon_1 + \varepsilon_2)}.$$ (2.171)

1251

1252 At ω_{max} the value of ε' from eq. (2.169) is $\lim_{\phi \to 0} \varepsilon' = \varepsilon_2$ that when combined with eq. (2.170)

1253 produces eq. (2.164).

1254
1255 2.3.7   Examples
1256   Attention is restricted to the dielectric relaxation of water molecules in different
1257 environments.
1258
1259 2.3.7.1 Liquid Water
1260   Water is one of the few liquids that relaxes with a single retardation time (or very close to
1261 it) and therefore has a Debye complex permittivity. Its dielectric relaxation frequency depends on
1262 temperature but always lies within the microwave region of the em spectrum. This has important
1263 implications for both navigational and meteorological radar and is of course the basis for
1264 microwave cooking. The temperature dependence of the retardation time is not Arrhenius but
1265 rather adheres to the empirical Fulcher equation (1.543) and (2.150), repeated here for
1266 convenience:
1267

1268 $$\tau = A_F \exp\left(\frac{B_F}{T - T_0}\right),$$ (2.172)

1269

1270 with parameters $A_F = 1.25 \times 10^{-13}$ s, $B_F = 669$ K, $T_0 = 138$ K that give a good description of $\tau(T)$

1271 down to the limit of supercooling of bulk water, ca. -35^0 C. The relaxation frequency $(1/2\pi\tau)$

1272 therefore varies between 62 GHz at 0° C and 74 GHz at 100 ^{o}C and the energy absorption at 100

1273 ^{o}C is about 75% that at 0 ^{o}C. Microwave ovens generally operate at a frequency 2.45 GHz that

1274 lies on the low frequency side of the Debye dielectric loss peak - the dielectric losses at this

1275 frequency are about 4.0% and 3.3% of the maximum loss. The fact that the frequency of a

1276 microwave oven is on the lower side of the dielectric loss peak of water means that energy
1277 absorption decreases with increasing temperature as the loss peak moves to higher frequencies,
1278 thus preventing runaway heating.
1279
1280 2.3.7.2 Supercooled Water
1281   Maxwell-Wagner polarization has been used to obtain the relative permittivity of
1282 supercooled water down to about -35^0C [37, 38]. The Maxwell-Wagner losses occur in the
1283 frequency range $10^5 - 10^6$ Hz that is far below the frequency range for the dielectric relaxation of
1284 water (around 10^{11} Hz) so that the measured values for the relative permittivity correspond to the
1285 limiting low frequency value $\varepsilon_0 >: 80$. This range is also far above the relaxation frequency for
1286 ice that is about $10^{3.5}$ Hz at 0°C and decreases with decreasing temperature, so that if
1287 crystallization occurred the relevant relative permittivity of ice is the limiting high frequency
1288 value $\varepsilon_\infty : 5$, far smaller than the limiting low frequency value $\varepsilon_0 >: 80$ It is fortunate that the
1289 Maxwell-Wagner losses occur at frequencies between the relaxation frequency ranges of water
1290 and ice and do not overlap with either.
1291   Emulsions of water in heptane stabilized by the surfactant sorbitol tristearate [37] and
1292 droplets suspended in beeswax [38] both exhibit Maxwell-Wagner polarization. In the first and
1293 rigorous beeswax study by Hasted and Shahidi [38] volume fractions of 0.5% and 1.0% were
1294 used. Hodge and Angell [37] later used a much larger volume fraction of water (30%) that was
1295 necessitated by their much lower instrumental sensitivity. Their data were stated to be
1296 inconsistent with the Maxwell-Wagner formulae because the observed values of ε''_{max} were
1297 claimed to be about four times larger than predicted and their sign of $(d\varepsilon''_{max}/dT) \propto (d\varepsilon_1/dT)$ was
1298 positive rather than negative as predicted by their eq. (3). However their eq. (3) is incorrect – the
1299 numerator term ε_2^2 of eq. (2.170) was given as ε_1^2 so that the analyses of ε^*_{MW} given in [1] and
1300 [37] are both incorrect. Equation (2.170) predicts that ε''_{max} is indeed inversely proportional to ε_1
1301 if $\varepsilon_1 ? \varepsilon_2$ (a good approximation for water droplets in hexane). The analyses in terms of the
1302 electric modulus [1,37] are unaffected by this mistake and remain valid although the stated
1303 requirement that a series capacitance that simulates the surfactant layer around the droplet needs
1304 to be large for the modulus analysis to be useful [1] is not correct (see eq. (2.107) above).
1305   The observed maxima in ε'' decreased with decreasing temperature that is consistent with
1306 eq. (2.170), but for $\varepsilon_1 \approx 100 ? \varepsilon_2 \approx 2$ and $\phi = 0.3$ the predicted value is about
1307 $\varepsilon''_{max} \approx \{(9)(0.3)(4)/[2(106)]\} \approx 0.005$, compared with the experimental values that range
1308 between about $0.4 - 0.8$. The observed value is therefore too large by a factor of about 100. Also,
1309 the measured ratio of ε''_{max} at the temperature extremes of 0°C and -35°C is about 1.8 compared
1310 with the correct value of about 1.2. The observed values of ω_{max} for ε'' were centered
1311 around $2\pi(5.5 \times 10^6 Hz) \approx 3.5 \times 10^7$ rad/s from which eq. (2.171) predicts a conductivity of about
1312 $\sigma_1 \approx e_0 \left[(2\varepsilon_1 + \varepsilon_2) + \phi(\varepsilon_1 - \varepsilon_2)\right] \omega_{max}/(1-\phi) \approx (9 \times 10^{-12} \text{ F/m})(230)(3.5 \times 10^7)/0.7$
1313 $\approx (9 \times 10^{-12} \text{ F/m})(230)(3.5 \times 10^7)/0.7 \approx 0.1 \text{ S/m}$, that is impossibly high.
1314   The measured modulus peak heights also decreased with decreasing temperature and since

1315 $M"_{max}$ is assumed to be inversely proportional to the permittivity this trend is also in the correct
1316   direction. Values of ε_1 for water were then derived by assuming that $M"_{max} \propto 1/\varepsilon_1$, fixing the
1317   proportionality constant from literature data for ε_1 at $0\ ^{0}$C and then least squares fitting a
1318   quadratic in temperature to eight data points between 0^{0}C and $-35\ ^{0}$C. Agreement with the earlier
1319   results, of which the authors were unaware at the time of paper submission (see *Note added in*
1320   *Proof* in [37]), was within the $\pm 2\%$ uncertainties claimed for each method but the agreement is
1321   better than this because most of the discrepancies are systematic due to the different values of ε_1
1322   at 0°C for the two methods (measured in [38] but chosen from the literature as a proportionality
1323   constant in [37]). When this is corrected for by equating the average of the modulus derived
1324   permittivities to the average from reference [38] the differences are reduced to 0.5% or less. This
1325   is a remarkable result given the simplifications used in the modulus analysis.
1326   These Maxwell-Wagner results can be rationalized in terms of a simplified equivalent
1327   circuit for the emulsified water droplets: a parallel (R_1C_1) element (corresponding to the water
1328   droplet with relative permittivity ε_1 and conductivity σ_1) is in series with a capacitance C_s that
1329   simulates the suspected thin layer of emulsifier, and a capacitance C_2 in parallel with the series
1330   combination to simulate the surrounding heptane. Intuitively C_2 is much smaller than C_1 from
1331   both geometrical and physical considerations $(\varepsilon_2 = \varepsilon_1)$. The circuit analysis is:

1332   (i)   Admittance A_1 of parallel (R_1C_1) element:

1333 $A_1 = 1/R_1 + i\omega C_1 = (1 + i\omega R_1 C_1)/R_1 = (1 + i\omega\tau_1)/R_1$ so that

1334

1335 $Z_1 = R_1/(1 + i\omega\tau_1).$ (2.173)

1336

1337   (ii)   Impedance of $\{(R_1C_1) + C_s\}$ arm $= Z_{1s} = \dfrac{R_1}{1 + i\omega\tau_1} + \dfrac{1}{i\omega C_s} = \dfrac{i\omega R_1 C_s + 1 + i\omega\tau_1}{i\omega C_s(1 + i\omega\tau_1)} \Rightarrow$

1338

1339 $A_{1s} = \dfrac{i\omega C_s(1 + i\omega\tau_1)}{1 + i\omega(\tau_1 + R_1 C_s)}.$ (2.174)

1340

1341   (iii)   Admittance A_{1s2} of complete circuit:

1342 $A_{1s2} = A_{1s} + i\omega C_2 = \dfrac{i\omega C_s - \omega^2 C_s\tau_1 + i\omega C_2\left[1 + i\omega(\tau_1 + R_1 C_s)\right]}{1 + i\omega(\tau_1 + R_1 C_s)} =$

1343

1344 $\dfrac{i\omega(C_s + C_2) - \omega^2\left(C_s\tau_1 + C_2\tau_1 - R_1 C_s C_2\right)}{1 + i\omega(\tau_1 + R_1 C_s)}.$ (2.175)

1345

1346   (iv)   For $C_2 = C_1$ appropriate for water droplets in heptane the total admittance simplifies to

1347

1348 $$A_{1s2} = \frac{i\omega C_s - \omega^2 R_1 C_1 C_s}{1 + i\omega R_1 (C_1 + C_s)}.$$ (2.176)

1349
1350 Thus
1351

1352 $$C_{1s2}^* = \frac{A_{1s2}}{i\omega} = \frac{C_s(1 + i\omega R_1 C_1)}{1 + i\omega R_1 C_s} = \frac{C_s(1 + i\omega R_1 C_1)(1 + i\omega R_1 C_s)}{1 + \omega^2 R_1^2 C_s^2}$$
$$= \frac{C_s - \omega^2 R_1^2 C_1 C_s}{1 + \omega^2 R_1^2 C_s^2} + \frac{i\omega C_s R_1(C_1 + C_s)}{1 + \omega^2 R_1^2 C_s^2}$$ (2.177)

1353
1354 so that
1355

1356 $$C'' = \frac{\omega C_s R_1(C_1 + C_s)}{1 + \omega^2 R_1^2 C_s^2}.$$ (2.178)

1357
1358 The maximum value $(C_1 + C_s)/2$ for C'' is therefore determined in part by the surfactant layer
1359 and is greater than the value $C_1/2$ for no series capacitance. This is consistent with the observed
1360 maxima in ε'' [37] being about 100 times greater than that calculated from the Maxwell-Wagner
1361 expression. The maximum in C'' also occurs at $\omega_{max} = 1/(R_1 C_s)$ that is also determined in part by
1362 the surfactant layer and therefore would give an incorrect value for the conductivity of water. This
1363 dependency of the relaxation time on C_s can also account for the (unreported) fact that changing
1364 the suspending medium changed ω_{max} [37] since the suspending medium would be expected to
1365 affect the surfactant layer and C_s.
1366   The imaginary component of the electric modulus for the same circuit when $C_2 = C_1$ is
1367

1368 $$M'' = \frac{i\omega R_1}{\left(1 + i\omega^2 R_1^2 C_1^2\right)} = \left(\frac{1}{C_1}\right) \frac{i\omega R_1 C_1}{\left(1 + i\omega^2 R_1^2 C_1^2\right)},$$ (2.179)

1369
1370 the maximum value of which is $1/(2C_1)$ and therefore contains the desired information about C_1
1371 that is independent of C_s. The frequency of maximum M'' is $\omega_{max} = 1/(R_1 C_1)$ and is also
1372 independent of C_s.
1373   Matlab® and GNUOctave calculations of the relaxation functions for the circuit enable
1374 values of the circuit elements to be quickly estimated that produce trends that are generally
1375 consistent with the experimental data, with the notable exception of the maximum values of ε''
1376 (discussed briefly below). For example good agreement with the experimental trends is attained
1377 with $R_1 = 10^3\,\Omega$; $C_1 = 10^{-3}\,\text{F}$; $C_2 = 10^{-5}\,\text{F}$; $C_s = 5 \times 10^{-4}\,\text{F}$. The value of 100 for the ratio C_1/C_2
1378 was chosen to approximate the ratio of permittivities of water and hexane and to accommodate an
1379 unknown geometric factor for the suspending medium relative to the droplet, and the value of C_s

1380   was found from the experimental ratio of 0.5 for the frequencies of maximum ε'' and M'' (the
1381   latter being higher). The geometric factor is probably the largest source of uncertainty in
1382   estimating the values of the circuit parameters.
1383   The Maxwell-Wagner equivalent circuit discussed here is obviously crude but serves to
1384   rationalize the remarkable success of the electric modulus in analyzing the Maxwell-Wagner
1385   effect for water droplets in a dielectric medium of low permittivity.
1386
1387   2.3.7.3 Hydration Water
1388   Water of ionic hydration is readily probed by dielectric relaxation if the ionic conductivity
1389   contribution to ε'' and $\tan\delta$ is sufficiently small, such as often occurs in hydrate glasses. Data for
1390 $Ca(NO_3)_2$ hydrate glasses [39] provide a convenient illustration of how water in different
1391   molecular environments can be distinguished dielectrically. Spectra of dielectric $\tan\delta$ vs. $1/T$ at
1392   1 Hz were shown for eight glasses of composition $Ca(NO_3)_2.RH_2O$ (R = 3, 4, 5, 6, 8, 10, 12,
1393   14). Glasses with lower R values required the addition of KNO_3 to ensure glass formation but this
1394   was expected to have only a minor effect on water dynamics because water was expected to be
1395   much more strongly bound to Ca^{2+} because of its larger ionic charge/radius compared with K^+.
1396   Four relaxations were observed labeled as $\alpha, \beta, \gamma, \delta$:
1397 (α) A conductivity relaxation at low $1/T$ corresponding to the onset of conductivity at glass
1398   transition was manifested as a steep increase in $\tan\delta$. The relaxation temperature corresponds to
1399 $\tan\delta = 1$ and will be referred to here as the "conductivity wing". It is essential that this relaxation
1400   occur at sufficiently high T in order that the other relaxations occur in the poorly conducting
1401   glassy state and not be hidden beneath the conductivity contribution to $\tan\delta$.
1402 (β) A dielectric relaxation lying close to the conductivity wing whose shift in position with R
1403   paralleled that of the conductivity relaxation. It was observable only as a shoulder for $R = 1-6$
1404   and (probably) R = 10 but is seen as a distinct peak for $R \approx$ trace.
1405 (γ) A weak low temperature dielectric relaxation $\left(\tan\delta_{max} \approx 10^{-3} - 10^{-2}\right)$ was observed as a
1406   broad maximum for R = 4, 5, 6 and as a shoulder for $R \geq 8$.
1407 (δ) A dielectric relaxation whose intensity increased rapidly with R. It was probably a part of
1408   the broad maximum near $10^3/T \approx 7.5$ for R = 8 but appeared as a clear maximum for $R \geq 10$.
1409   The β relaxation was assigned to cation bound water that for the reason given above
1410   probably coordinates Ca^+ rather than K^+. The rapid shift in relaxation temperature with $R > 1$ was
1411   interpreted as a change in water dynamics as H_2O replaces NO_3^- in the first coordination shell of
1412 Ca^+. The R - invariance for R = trace and R = 1 was attributed to a single water molecule lying in
1413   the first coordination shell. This assignment of the β relaxation to Ca^{2+} bound water implied a
1414   dielectric activity that merits discussion. The most plausible geometry for H_2O coordinated to Ca^+
1415   is when the H_2O dipole points away from the Ca+ ion. However if this held in the complex ionic
1416   environment of the glass there would be no dielectric activity because the rotational axis would
1417   bisect the H-O-H angle and coincide with the dipole vector. Two alternatives suggest themselves:
1418   (1)   Exchange of water and nitrate in the coordination shell. This implies an associated volume
1419   fluctuation and ultrasonic activity. Such activity has been observed [40,41] in $Ca(NO_3)_2 \cdot RH_2O$

1420   solutions at about 20 MHz at room temperature. This relaxation moved to higher frequencies with
1421   increasing R and the edge of a second relaxation at higher frequencies was noted, both being
1422   consistent with the glassy state dielectric behavior. Such an exchange would also be expected to
1423   contribute to the translational ionic migration that produces conductivity, consistent with the
1424   essentially R – invariant difference between the α and β relaxation temperatures. The
1425   possibility that this relaxation is part of a conductivity relaxation with a distribution of relaxation
1426   times is discussed in §2.5.
1427   (2)   A different Ca^{+}-OH_2 geometry in which the dipole vector and rotation axis do not
1428   coincide. Neutron diffraction data indicate this occurs in $CaCl_2$ and $NiCl_2$ solutions [42], in
1429   which an angle of ca. 40° was observed between the dipole and coordination axes at $R = 12.6$
1430 $\left(NiCl_2 \right)$ and 12.3 $\left(CaCl_2 \right)$, and about 0° in dilute solutions $\left(R \approx 450 \right)$. It was not possible to find
1431   the dielectric activity per water molecule of the β relaxation in the $Ca(NO_3)_2 \cdot RH_2O$ glasses
1432   because of overlap with the conductivity wing and the γ relaxation, but for the mixed nitrate
1433   glasses the well defined conductivity wing for the anhydrous mixture could be shifted and
1434   subtracted to yield plausibly shaped peaks of $\tan\delta$ vs. $1/T$. The peak heights and widths in the R
1435   = 1 and $R = 3$ glasses were about the same so that barring an unlikely ratio of activation energies
1436   in excess of 3 it appears that the dielectric activity per water molecule does indeed decrease with
1437   increasing R. A crude calculation yielded sensible values of $\Delta\theta$ from the observed values of
1438 $\tan\delta_{max}$: the dipole being relaxed was assumed to be the component of the water dipole $\left(\mu_W \right)$
1439   orthogonal to the rotation axis, magnitude $\mu_W \sin(\Delta\theta)$, and $\tan\delta_{max}$ was assumed to be
1440   proportional to $\left(\varepsilon_0 - \varepsilon_\infty \right)$ that is in turn proportional to $R\left[\mu_W \sin(\Delta\theta) \right]^2$. Equating $\tan\delta_{max}$ for
1441   the $1R$ and $3R$ glasses then yielded
1442
1443
$$\frac{3}{T_{3R}} \sin^2\left(\Delta\theta_{3R} \right) = \frac{1}{T_{1R}} \sin^2\left(\Delta\theta_{1R} \right),$$
(2.180)
1444
1445   so that
1446
1447
$$\sin^2\left(\Delta\theta_{3R} \right) \approx 0.286 \sin^2\left(\Delta\theta_{1R} \right).$$
(2.181)
1448
1449   Examples of $\left\{ \Delta\theta_{1R}, \Delta\theta_{3R} \right\}$ pairs were $\left\{ 60^0, 28^0 \right\}$ and $\left\{ 30^0, 15^0 \right\}$, both sensible values and roughly
1450   comparable with the neutron diffraction values.
1451   For large values of R the δ relaxation was expected to resemble that of pure water so that
1452   an extrapolation to infinite dilution could yield the temperature at which the relaxation frequency
1453   of water is 1 Hz. The retardation temperatures at 1 Hz for the δ relaxation in four glasses
1454   (Ca(NO3)2, CaZnCl4, Li2ZnCl4 and ZnCl2 hydrates) all extrapolated to 162 ± 5 K at infinite
1455   dilution, suggesting that the relaxation temperature for pure water would be 162 ± 5 K at 1Hz.
1456   The temperature dependence of the relaxation time for water between -20^oC to $+30^o$C [43] was
1457   found to follow the Fulcher equation
1458

1459 $$\tau(T) = A_F \exp\left(\frac{B_F}{T - T_0}\right) \tag{2.182}$$

1460

1461 with $A_F = 1.25 \times 10^{-13}$ s, $B_F = 669$ K, $T_0 = 138$ K. The extrapolated {1 Hz, 162 ± 5 K} datum
1462 agreed with the predicted Fulcher value {1 Hz, 162 K}. Given the large extrapolation over about
1463 11 orders of magnitude (!) this agreement constitutes good evidence that dielectric relaxation of
1464 water outside the first coordination shell of the Ca^{2+} and Li^+ cations is the same as pure water.
1465 This was supported by a similar extrapolation of LiCl in glycerol data that yielded a relaxation
1466 temperature equal to the directly observable value for pure glycerol at 1 Hz.
1467

1468 2.4   Conductivity Relaxation
1469 2.4.1   General Aspects
1470   As noted earlier relaxation of polarization can occur either by translation of electric charge
1471 (electric current), or by dipole rotation/localized ion hopping (displacement current). Thus
1472 polarization induced by an electric field can occur by *conductivity relaxation* [44] arising from
1473 long range translational migration of point charges as well as by the dielectric relaxation
1474 considered so far. The time scale associated with a frequency invariant conductivity σ_0 is defined
1475 by (eq. 1.42)
1476

1477 $$\langle \tau_D \rangle = \sigma_0 / e_0 \varepsilon_\infty, \tag{2.183}$$

1478

1479 but this is not evident in σ' vs $\ln\omega$ plots nor is it for the function $\varepsilon^* = \varepsilon' - i\sigma_0 / e_0\omega$. However
1480 ρ'' and M'' clearly indicate the time scale because they exhibit maxima in the frequency domain
1481 at $\omega \approx 1/\langle \tau_D \rangle$. The time constant τ_D in eq. (2.183) differs from the characteristic time τ_e in the
1482 Fermi gas expression for electronic conductivity in metals that is directly proportional to σ_0 [45]:
1483

1484 $$\tau_e = \frac{m}{ne^2} \sigma_0, \tag{2.184}$$

1485

1486 where n is the number density of charge carriers of effective mass m and charge e. The reason for
1487 the difference is that τ_e is the average time of travel between *scattering events* (collisions with
1488 ions, electrons, phonons or by umklapp), whereas τ_D is the residence time between (effectively
1489 instantaneous) *jumps between adjacent sites*. Nor is τ_D equal to τ_E for dielectric relaxation,
1490 although they are related by an expression that is derived below.
1491   Equation (2.183) implies that ionic conductivity cannot exceed ca. 10^3 Sm^{-1}, since τ_D
1492 cannot reasonably be less than a vibrational lifetime τ_v and ε_∞ is rarely greater than about 10.
1493 The vibrational lifetime is conveniently defined by the condition for critical damping (§1.11),
1494 $\omega_0 \tau_v = 1$, so that for a typical vibrational frequency of about $f \approx 10^{12}$ Hz $\Rightarrow \omega \approx 6 \times 10^{12}$ rad/s the

1495   value of τ_v is about 2×10^{-13} s and

1496

1497 $$\sigma_{0,max} \approx \frac{e_0 \varepsilon_\infty}{\tau_V} \approx \frac{\left(8.854 \times 10^{-12} \text{ F/m}\right)(10)}{2 \times 10^{-13} \text{ s}} \approx 450 \text{ S/m},$$ (2.185)

1498

1499   comparable with the highest conductivity observed for ionic conductors.

1500   The properties of the four basic functions for conductivity relaxation (eq. (2.106)) are

1501   conveniently illustrated using a circuit comprising three elements in series: (i) a capacitance

1502 $C_s = 10^{-6} \text{ F} = 1\mu\text{F}$; (ii) a parallel combination of a resistance $R_1 = 10^8 \ \Omega$ and capacitance

1503 $C_1 = 10^{-12} \text{ F}(1\text{pF})$ (iii) another parallel combination of a resistance $R_2 = 10^6 \ \Omega$ and capacitance

1504 $C_1 = 10^{-12} \text{ F}(1\text{pF})$. The two parallel R_p-C_p elements could for example simulate crystal and inter-

1505   crystal impedances in a polycrystalline samples and the series capacitance C_s could simulate

1506   electrode polarization. As discussed below this circuit has been used by several groups and will

1507   be referred to as the "ideal" conductivity circuit.

1508   The electric modulus $M^* = M' + iM''$ is particularly useful for analyzing conductivity

1509   relaxation but it is controversial (a discussion of many of the issues is given in [1]). It was

1510   probably first defined by McCrum, Read and Williams [32], but its use in analyzing conductivity

1511   relaxation was initiated by Macedo and coworkers [44]. The usefulness of M^* is illustrated by the

1512   simplest case of a constant conductivity σ_0 and constant relative permittivity ε_∞ (the reason for

1513   the subscripts will become clear when distribution functions are considered later). Consider the

1514   definitions

1515

1516 $$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \qquad \text{(a)},$$

$$M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \qquad \text{(b)}.$$ (2.186)

1517

1518   Insertion of the relations $\varepsilon'' = \sigma_0 / e_0 \omega$ and $\varepsilon' = \varepsilon_\infty$ then yields

1519

1520 $$M' = \frac{1}{\varepsilon_\infty^D}\left(\frac{\omega^2 \tau_D^2}{1 + \omega^2 \tau_D^2}\right)$$ (2.187)

1521

1522   and

1523

1524 $$M'' = \frac{1}{\varepsilon_\infty^D}\left(\frac{\omega \tau_D}{1 + \omega^2 \tau_D^2}\right).$$ (2.188)

1525

1526   Thus M'' exhibits a desirable peak centered at $\omega_D = 1/\tau_D$ as a function of $\ln(\omega)$. The components

1527   of the complex resistivity ρ^* are related to those of M^* by (eq. (2.106))

1528

1529 $$\rho' = \frac{M''}{e_0 \omega} = \frac{\tau_D}{e_0\, \varepsilon_\infty^D}\left(\frac{1}{1+\omega^2\tau_D^2}\right) = \left(\frac{\rho_0}{1+\omega^2\tau_D^2}\right) \qquad (2.189)$$

1530
1531 and
1532

1533 $$\rho'' = \frac{M'}{e_0\,\omega} = \frac{\tau_D}{e_0\,\varepsilon_\infty^D}\left(\frac{\omega\tau_D}{1+\omega^2\tau_D^2}\right) = \rho_0\left(\frac{\omega\tau_D}{1+\omega^2\tau_D^2}\right), \qquad (2.190)$$

1534

1535 where $\rho_0 = 1/\sigma_0 = \tau_D / e_0\varepsilon_\infty^D$. The functions M'' and ρ'' have identical frequency dependencies
1536 but are weighted by $1/\varepsilon_\infty$ and ρ_0 respectively. The difference in weighting factors can be exploited
1537 to considerable advantage in the analysis of ac conductivity data (§2.3.5.6 - §2.3.5.8).
1538   For dielectric relaxation M^* and ε^* are almost equivalent because a Debye peak in ε''
1539 also yields a Debye peak in M'' [44] [see eqs. (2.132) and (2.133)]. The derivation of M^* for a
1540 Debye dielectric without any conductivity is given in Appendix 2.1. It might appear that a peak in
1541 M'' could be due to either a conductivity or dielectric process and that M^* could not distinguish
1542 between them but this is not necessarily so because the average relaxation time $\langle\tau_D\rangle$ will be
1543 calculable from the limiting low frequency conductivity [eq. (2.73)] if the process is a
1544 conductivity relaxation, and the retardation time will not correlate with σ_0 .if the peak in M'' is
1545 due to a dielectric relaxation Also $\lim_{\omega\to 0} M'(\omega) = 1/\varepsilon_0$ for dielectric relaxation compared with
1546 $\lim_{\omega\to 0} M'_{conductivity}(\omega) = 0$ for conductivity relaxation. The archetypal example of dielectric
1547 relaxation being correlated with σ_0 occurs in the alkali silicate glasses and it was this correlation
1548 that originally led to the inference that the residual dielectric loss (after subtraction of $\sigma_0 / e_0\omega$) is
1549 due to the same alkali migration process that produces σ_0 [27-31]. This led Macedo and
1550 collaborators [44] to first use M^* in the analysis of conductivity relaxation.
1551   The low frequency conductivity relaxation limit for M' is revealing because M' is a
1552 measure of the restoring force in response to an electric field perturbation. The low frequency
1553 limit of this restoring force is finite for dielectric relaxation because the charge storage ability
1554 remains nonzero: $\lim_{\omega\to\infty} \varepsilon'(\omega) = \varepsilon_0$. For conductivity relaxation the dielectric loss becomes infinite
1555 as $\omega \to 0$ (dissipation completely overrides any storage capability) and the restoring force is
1556 "short circuited". This is precisely analogous to the mechanical modulus going to zero as the
1557 viscosity of a viscoelastic material dominates at low frequency and the elasticity disappears. The
1558 electric modulus was first introduced to emphasize this mechanical analogy [32].
1559   An alternative to the electric modulus for analyzing materials in which the dielectric loss
1560 and conductivity are correlated has been proposed by Johari [46]. This proposal is similar in style
1561 to a mechanism for ionic conductivity proposed by Hodge and Angell [47] that was based on the
1562 one-dimensional Glarum diffusion model for dielectric relaxation [§1.12.6, Chapter One]. The
1563 Glarum model comprises a relaxing dipole that can relax either independently with retardation
1564 time τ_0 or by the arrival of a defect of some kind that relaxes it instantly. Hodge and Angell
1565 suggested that the dipole is a trapped ion/vacancy pair (known to exhibit Debye dielectric

1566   behavior, §2.3.1.2) and that the defects are itinerant ions that contribute to σ_0. Such diffusing
1567   ions would eliminate the dipole upon arriving by inserting themselves into the vacancy, consistent
1568   with the Glarum model. The average activation energy for oscillation of trapped ions and that for
1569   ion migration are presumed to be similar (perhaps identical), thus accounting for the nearly
1570   temperature invariant distribution of conductivity relaxation times. The Glarum function is
1571   mathematically similar to the Davidson-Cole function that has a (rarely observed) Debye-like low
1572   frequency loss. This low frequency behavior arises from the Glarum assumption that the dipole
1573   has just one retardation time. However if a distribution of dipole retardation times is assumed,
1574   corresponding to a distribution of sites in an amorphous material and/or local fields effects
1575   (§2.3.1.2) for example, better agreement with experiment might be obtained without changing the
1576   essential physics of the Glarum model.
1577
1578   2.4.2   Distribution of Conductivity Relaxation Times
1579   Both M^* and ρ^* can be formally described in terms of a distribution of conductivity
1580   relaxation times:
1581

$$M^*(i\omega) = M_\infty \int_{-\infty}^{+\infty} g\left(\ln \tau_D\right)\left(\frac{i\omega\tau_E}{1+\omega^2\tau_D^2}\right)d\ln\tau_D \qquad (2.191)$$

1583
1584   and similarly for $\rho^*(i\omega)$. A distribution of conductivity relaxation times affects the dispersion
1585   of the corresponding complex admittance functions $\varepsilon^*(i\omega)$ and $\sigma^*(i\omega)$:
1586

$$\sigma_0 = \frac{e_0 \varepsilon_\infty^D}{\langle \tau_D \rangle} = \frac{e_0}{M_\infty^D \langle \tau_D \rangle}, \qquad (2.192)$$

$$\sigma_\infty = e_0 \varepsilon_\infty^D \left\langle \frac{1}{\tau_D} \right\rangle = \frac{e_0}{M_\infty^D}\left\langle \frac{1}{\tau_D} \right\rangle, \qquad (2.193)$$

1589
1590   and
1591

$$\varepsilon_0^D = \varepsilon_\infty^D \frac{\langle \tau_D^2 \rangle}{\langle \tau_D \rangle^2} \geq \varepsilon_\infty^D. \qquad (2.194)$$

1593
1594   A distribution of conductivity relaxation times is not easily distinguishable from dielectric
1595   and conductivity relaxations occurring together [36,44], although the dielectric relaxation will not
1596   be observable if τ_E ? τ_D because σ_0 will then exceed the limiting high frequency dielectric
1597   conductivity given by eq. (2.131):
1598

1599
$$\frac{\sigma'(\omega\tau_D \to 0)}{\sigma_\mu'(\omega\tau_E \to \infty)} = \frac{\sigma_0}{\sigma_\mu(\infty)} = \frac{\varepsilon_\infty}{\langle\tau_D\rangle}\left(\frac{\langle\tau_E\rangle}{\varepsilon_0 - \varepsilon_\infty}\right) = \frac{\varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty}\frac{\langle\tau_E\rangle}{\langle\tau_D\rangle} \gg 1.$$
(2.195)

1600

1601 This phenomenon has been directly observed in systems for which the dielectric retardation time
1602 is essentially constant but whose conductivity is increased by addition of electrolyte [48, 49] (also
1603 see §2.3.6.9 below).

1604

1605 2.4.3   Constant Phase Element Analysis
1606   It is sometimes useful to have a circuit element for which the phase angle is independent
1607 of ω,

1608

1609
$$W^*(i\omega) = W(\omega)\exp\left(\frac{\pm i\,\alpha\pi}{2}\right),$$
(2.196)

1610

1611 where $W(\omega)$ is any real function and $0 < \alpha \le 1$ is also real (the positive sign in the exponent
1612 corresponds to an admittance and the negative sign to an impedance). However as noted in
1613 Chapter One and §2.4.3 eq. (2.196) can only be valid over a restricted frequency range because
1614 otherwise the underlying distribution of relaxation/retardation times cannot be normalized.
1615 Equation (2.196) is a generalization of the Warburg impedance for which $\alpha = 0.5$.

1616

1617 2.4.4   Estimation of σ_0

1618   Several methods have been published for estimating σ_0 in situations where it has been
1619 contaminated by such factors as electrode polarization and intergranular impedances. An accurate
1620 value for σ_0 is often important because, in addition to the obvious need for reliable data, its
1621 contribution to ε'' must be subtracted for permittivity analyses (the attendant difficulties have
1622 been discussed by Ravaine and Souquet [52, 53]). Accurate values of σ_0 are also needed in order
1623 to determine reliable activation energies for conductivity. For example if $\log(\sigma)$ measured at
1624 constant measuring frequency ω_{meas} is plotted against $1/T$ in the usual Arrhenius fashion then
1625 spurious changes in slope can result from both electrode polarization and bulk relaxation effects.
1626 (1)   If the measuring frequency ω_{meas} is so low that polarization is significant then the
1627 measured conductivity will be less than σ_0, by an amount that increases with increasing
1628 temperature because of the shift to higher frequencies of the polarization σ' spectrum (which has
1629 essentially the same effective activation energy as the sample conductivity).
1630 (2)   A fictitiously low activation energy is then obtained at high temperatures as ω_{meas} probes
1631 deeper into the polarization relaxation. A spuriously low activation energy can also occur at low
1632 temperatures when ω_{meas} lies within the bulk relaxation frequency range where σ' is often
1633 observed to increase as ω^α $(\alpha < 1)$. In this case the measured conductivity will exceed σ_0 by an
1634 amount that decreases with increasing temperature and the measured activation energy will be
1635 smaller than the true value by the factor $\alpha = d\ln\sigma'/d\ln\omega$:

1636

1637 $$E_{a,obs} = E_{a,true}\left(1-\alpha\right).$$ (2.197)

1638

1639   In cases where $\alpha \approx 1$, as occurs in some electronic semiconductors [48], the fixed frequency
1640   conductivity is therefore almost independent of temperature in the bulk relaxation temperature
1641   region.

1642

1643   2.4.4.1 Analyses in the Complex Resistivity Plane
1644   Ravaine and Souquet [52,53] used the complex resistivity plane for determining σ_0 of
1645   alkali silicate glasses in the presence of electrode polarization using low frequency extrapolations
1646   to the real axis. They fitted the high frequency spectrum (i.e. sample relaxation) to the Cole-Cole
1647   [54] function (§1.12.5) and extrapolated the Cole-Cole semicircle to the real axis. For severe
1648   polarization Armstrong et al. [55-59] used a similar method based on extrapolation of the high
1649   frequency polarization spike to the real axis. This method is restricted to high conductivities
1650   whose relaxation frequency lies above the measuring frequency range.

1651

1652   2.4.4.2 Modulus and Resistivity Spectra
1653   In cases where electrode polarization and conductivity relaxations overlap significantly
1654   and no plateau in σ' is observed, σ_0 can be estimated from eq. (2.183) if $\langle \tau_D \rangle$ and ε_∞ are known.

1655   These can sometimes be determined with sufficient precision by fitting $M''(\omega)$ to an appropriate
1656   empirical function because M'' is insensitive to high capacitance effects such as electrode
1657   polarization and intergranular impedances so that only the bulk relaxation is included in the fitted
1658   function. For this application the fit to M'' should preferably be weighted by the lower frequency
1659   data because these reflect the longer relaxation time components of the distribution that contribute
1660   more significantly to $\langle \tau_D \rangle$. The maximum in ρ'', ρ''_{max}, can also be used to estimate σ_0 to within
1661   about 10% if the full width at half height of the peak in ρ'' (Δ decades) can be determined:

1662

1663 $$\sigma_0 \approx \frac{1}{1.75 \Delta \rho''_{max}}.$$ (2.198)

1664

1665   If only the maximum in ρ'' at ω_{max} is observable σ_0 can still be estimated from the value of ρ'
1666   at ω_{max} by assuming $\rho''(\ln \omega)$ to be symmetric:

1667

1668 $$\sigma_0 \approx \frac{1}{2\rho'(\omega_{max})}.$$ (2.199)

1669

1670   2.4.4.3 Complex Admittance Plane
1671   One of the first applications of complex plane plots was to polycrystalline yttria-zirconia
1672   electrolytes by Bauerle [60]. Bauerle gave an excellent discussion of equivalent circuits and their
1673   corresponding complex admittance plane plots, but the only circuit used in their data analysis was

1674   a series combination of two parallel R_pC_p elements and a series resistance R_s. The first parallel
1675 R_pC_p element in this circuit represented the electrode interface: the capacitance of a double layer
1676   in parallel with the resistance of an oxygen gas-oxide ion charge transfer process. The second
1677 R_pC_p element represented an intergranular boundary ("constriction") impedance, and the pure
1678   resistance simulated the bulk crystal. The experimentally observed complex admittance plane
1679   plots were in excellent agreement with the equivalent circuit predictions. The zero frequency
1680   conductivity predicted from the complex plane plot was also in excellent agreement with four
1681   terminal data, and the expected dependence of the electrode impedance on oxygen partial pressure
1682   was observed. Despite these successes, some disadvantages of the method should be pointed out.
1683   First, in assuming that the bulk crystal acts as a pure resistance the analysis implicitly assumes
1684   that the measuring frequencies are well below the conductivity relaxation frequency, that can only
1685   be confirmed retrospectively. Second, although there are three relaxing elements (since the
1686   sample resistance must realistically have a capacitance in parallel with it), the complex admittance
1687   plane exhibits only two arcs that reflect the differences between the relaxing elements. If the
1688   observed relaxations overlap significantly, an assumption must be made about the shapes of the
1689   two relaxations before extrapolations are made, i.e. a functional form for the extrapolating
1690   function must be chosen. Bauerle's data were well described by the Cole-Cole function but this
1691   would not be expected to occur in general.
1692

1693   2.4.5   Examples
1694   2.4.5.1 Electrode Polarization and Bulk Relaxation in the Frequency Domain
1695   Consider an "ideal" equivalent circuit similar to that used by Bauerle except that the series
1696   resistance is replaced by a series capacitance, with specific values of the parallel R_pC_p elements
1697   being $\left[R_1 = 10^8\,\Omega, C_1 = 10^{-11}\,\mathrm{F} \Rightarrow \tau_1 = R_1C_1 = 10^{-3}\,\mathrm{s} \right]$, $\left[R_2 = 10^6\,\Omega, C_2 = 10^{-11}\,\mathrm{F} \Rightarrow \tau_2 = R_2C_2 = 10^{-5}\,\mathrm{s} \right]$
1698   and $\left[C_s = 10^{-6}\,\mathrm{F} \right]$. The distribution of conductivity relaxation times then comprises two delta
1699   functions at $\tau_1 = 10^{-3}\,\mathrm{s}$ and $\tau_2 = 10^{-5}\,\mathrm{s}$. The shorter relaxation time element simulates the crystal
1700   impedance in a polycrystalline preparation, the longer relaxation time element simulates an
1701   intergranular impedance, and the series capacitance simulates electrode polarization. This circuit
1702   has been found to be useful in analyzing the electric response of a variety of conducting materials,
1703   including a superionic conductor [61], an electronic semiconductor [62], and a normal ionic
1704   conductor [9]. The relaxation time averages are
1705

1706 $$\langle \tau_D^2 \rangle = \frac{\tau_1^2 + \tau_2^2}{2} = 5.0005 \times 10^{-9}\ \mathrm{s} \qquad\qquad (2.200)$$

1707 $$\langle \tau_D \rangle = \frac{\tau_1 + \tau_2}{2} = 5.05 \times 10^{-5}\ \mathrm{s} \qquad\qquad (2.201)$$

1708 $$\langle \tau_D^{-1} \rangle = \frac{\tau_1^{-1} + \tau_2^{-1}}{2} = 5.05 \times 10^{+5}\ \mathrm{s} \qquad\qquad (2.202)$$

1709

1710   The high frequency relative permittivity is (assuming $k = 1$ for convenience so that $C_0 = e_0$
1711   numerically)
1712

1713 $$\varepsilon_\infty = \frac{C_1 C_2}{e_0 (C_1 + C_2)} = 5.647 \,, \tag{2.203}$$

1714
1715 and the low frequency relative permittivity is
1716

1717 $$\varepsilon_0 = \varepsilon_\infty \frac{\langle \tau_D^2 \rangle}{\langle \tau_D \rangle^2} = (5.647) \frac{(5.005 \times 10^{-9})}{(5.05 \times 10^{-5})^2} = 11.083 \,. \tag{2.204}$$

1718
1719 The limiting low and high frequency conductivities are
1720

1721 $$\sigma_0 = \frac{\epsilon_0 \varepsilon_\infty}{\langle \tau_D \rangle} = \frac{(8.854 \times 10^{-12})(5.647)}{(5.05 \times 10^{-5})} = 9.9 \times 10^{-7} \text{ S m}^{-1} \tag{2.205}$$

1722 $$\sigma_\infty = \epsilon_0 \varepsilon_\infty \langle 1/\tau_D \rangle = (8.854 \times 10^{-12})(5.647)(5.05 \times 10^{+5}) = 2.53 \times 10^{-5} \text{ S m}^{-1}. \tag{2.206}$$

1723
1724 (1) The ρ'' and M'' spectra both exhibit two peaks the heights of which reflect the different
1725 weighting of the two functions - eqs. (2.188) and (2.190). The two ρ'' peak heights differ by the
1726 ratio of the resistances $10^8 / 10^6 = 10^2$, whereas the M'' peaks are equal in height because the two
1727 capacitances are equal. If the capacitances were different and the resistances the same then the
1728 peaks in ρ'' would have the same height and those in M'' would differ. Also ρ'' increases
1729 indefinitely at low frequencies due to C_s whereas M'' is unaffected.
1730 (2) After subtraction of the contribution of σ_0 to ε'', and of the limiting high frequency
1731 contribution of ε_∞ to σ'', both σ'' and ε'' exhibit a single peak at a frequency between the two
1732 maxima exhibited in the M'' and ρ'' spectra. These single peaks in the admittance functions occur
1733 because at intermediate frequencies the high frequency RC element behaves as a resistance and
1734 the low frequency RC element behaves as a capacitance. As noted in §2.2.4 the effectively series
1735 RC circuit will produce just a single loss peak in the admittance. For the electrode polarization
1736 relaxation caused by C_s in series with the sample resistance $(R_1 + R_2)$ peaks in $\sigma'' - e_0 \varepsilon_\infty \omega$ and
1737 $\varepsilon'' - \sigma_0 / e_0 \omega$ are observed at lower frequencies.
1738 (3) A low frequency decrease in σ' and increases in ε' and ρ'' are found that are due to the
1739 electrode polarization simulated by C_s. For expositional clarity the value of C_s was chosen to
1740 ensure a clean separation between the simulated polarization and bulk relaxations but this does
1741 not occur in typical experimental data.
1742 (4) The complex plane plots have both advantages and disadvantages compared with the
1743 spectra. Two disadvantages are the inconvenience of locating the frequencies of maximum loss,
1744 and of comparing these frequencies in M^* and ρ^* plots because of the opposite directions of
1745 increasing frequency. On the other hand, complex plane plots are useful for extrapolations. For
1746 example in highly conducting materials whose conductivity relaxation frequency $1/\langle \tau_D \rangle$ lies
1747 above the measuring frequency, and for which electrode polarization is significant or even severe,

1748   the polarization spike in the $\rho*$ plane can be extrapolated to the real axis to give an estimate of

1749 $\sigma_0 = 1/\rho_0$. At frequencies above the conductivity relaxation frequency, σ_0 is manifested as a

1750   spike in the $\varepsilon*$ plane, corresponding to the limiting values of $\lim_{\omega\to 0}\varepsilon'' = \lim_{\omega\to 0}\sigma_0/\epsilon_0\omega = \infty$ and

1751 $\lim_{\omega\to 0}\varepsilon' = \varepsilon_0$.

1752

1753

1754   2.4.5.2 Conductivity Relaxation in Sodium β – Alumina

1755   Permittivity, modulus and resistivity spectra of single crystal sodium β-alumina at 113 K

1756   have been reported by Grant and Ingram [64,65]:

1757   (i)   the ε'' spectrum measured in the direction perpendicular to the conduction planes;

1758   (ii)   the M'' spectra in orientations perpendicular and parallel to the conducting planes;

1759   (iii)   the Z'' spectrum measured in the direction of the conduction planes.

1760   The frequency of maximum Z'' in the parallel orientation was close to the frequency of

1761   maxima in M'' and ε'' measured in the perpendicular orientation, and the activation energy for the

1762   parallel resistivity spectrum was close to that for the perpendicular dielectric loss spectrum. The

1763   data for the perpendicular orientation were interpreted in terms of a Maxwell layered dielectric

1764   [65], with each insulating spinel block being a capacitance and each conduction plane a

1765   resistance. The activation energy for the dielectric loss was thus determined by that of the

1766   conductivity of the conducting layers, that the data suggest is similar in directions parallel and

1767   perpendicular to the conduction planes. An extraordinarily large width of the M'' spectrum for

1768   single crystal Na β – alumina was observed in the parallel orientation [66,67], indicating a very

1769   broad distribution of conductivity relaxation times: the resistivity and modulus spectra taken

1770   together suggested that the distribution was bimodal. Grant and Ingram proposed that at 113 K the

1771   low frequency conductivity is determined by an activated localized ion motion that is the same in

1772   both orientations. The higher frequency conductivity, which contributed to M'' but not to ρ'',

1773   resulted from a relatively free motion of ions crossing low energy barriers. These processes were

1774   consistent with low temperature localization of sodium ions deduced from NMR data [68].

1775   Localized activation is not the rate determining step at high temperatures and the well-established

1776   low activation energy for conductivity in sodium β-alumina was observed. Spectra of M'' and Z''

1777   for a representative polycrystalline specimen at 113 K were also reorted. The Z'' spectrum was

1778   uninformative at this temperature, increasing monotonically at low frequencies due to electrode

1779   polarization. The M'' spectrum exhibited a maximum at about the same frequency as the single

1780   crystal M'' spectrum observed perpendicular to the conduction planes, and a reproducible shoulder

1781   was observed at about the same frequency as M'' observed parallel to the conduction planes in

1782   single crystals.

1783   This work demonstrates that comparison of the functions M'', ρ'' and ε'' can uncover

1784   details of the conductivity behavior of sodium β – alumina that could not even be discussed if

1785   only $\sigma*$ and $\varepsilon*$ data were used.

1786

1787   2.4.5.3 Complex Impedance Plane Analysis of Electrode Polarization in Sintered β –

1788   Alumina.

1789   The use of the complex impedance plane for extrapolating polarization phenomena to

1790 obtain data on the bulk material was used extensively by Armstrong and coworkers in their
1791 studies of superionic conductors such as Na β-alumina [55] and Ag-Rb iodide [54-58]. A spike
1792 in the complex impedance plane corresponds to the low frequency increase in Z'' due to the series
1793 electrode capacitance and extrapolation of this spike to the real axis yielded the limiting low
1794 frequency values of Z' and therefore of ρ_0. Different surface preparations were observed to
1795 affect the measured impedance but all of the extrapolations gave the same values for ρ_0. This
1796 method is clearly most appropriate for very highly conducting materials whose conductivity
1797 relaxation lies at frequencies well above those used experimentally.
1798
1799 2.4.5.4 Complex Impedance Plane Analysis of Atmosphere Dependent Electrode Effects in KHF$_2$
1800 Complex impedance plane analysis was also used by Bruinink and Broers [69] for the α
1801 and β phases of KHF$_2$. In an atmosphere of hydrogen with platinum paint electrodes, the complex
1802 impedance plane plot of data for α-KHF$_2$ was consistent with a Warburg impedance in parallel
1803 with the bulk resistance and capacitance [69], and extrapolation to the real axis gave a value of
1804 ρ_0 in agreement with a separately determined four terminal dc value. This plot gave no indication
1805 of interfacial polarization, consistent with α-KHF$_2$ being a proton conductor and the platinum
1806 paint electrodes behaving as reversible hydrogen electrodes. This contrasted sharply with the low
1807 frequency behavior of α-KHF$_2$ in a vacuum, where a double layer capacitance of about 440 mF
1808 m^{-2} per electrode in parallel with a Faradaic resistance of about $2\times10^4\,\Omega$m per electrode
1809 produced an additional semicircle in the complex plane. For the polycrystalline β-phase the
1810 complex plane plot was essentially unchanged for data taken in both a hydrogen atmosphere and a
1811 vacuum [69] and is consistent with a Warburg impedance in series with a parallel RC element,
1812 corresponding to electrode polarization due to blocking of K$^+$ and/or F$^-$ charge carriers. An RC
1813 transmission line was used to rationalize the Warburg impedance in terms of bulk electrical
1814 relaxation.
1815
1816 2.4.5.5 Intergranular Effects in Polycrystalline Electrolytes
1817 The effects of intergranular material on the overall electrical response of polycrystalline
1818 electrolytes have been extensively documented. Only one example is discussed here [9,66]. The
1819 simplest equivalent circuit representation of such materials comprises two parallel RC elements
1820 in series, where one element is associated with a crystallite and the other with intergranular
1821 material. Armstrong et al. [70] showed that such a series circuit can represent the principle
1822 features of polycrystalline electrolytes. Since the interface is thin and the permittivities of ionic
1823 solids typically vary by a factor of less than 10, the capacitance C_i associated with the interface is
1824 much higher than that of the grain C_p:
1825

1826 $$C_i = \frac{\epsilon_0\,\varepsilon'\,A_i}{d_i} \gg \epsilon_0\varepsilon' = k\,C_p \qquad (2.207)$$

1827
1828 where A_i is the average cross section area, d_i is the average thickness of the intergranular material,
1829 and $k = e_0\,/\,C_0$ is the cell constant.
1830

1831   2.4.5.6 Intergranular Cracking

1832   Experimental M'' and ρ'' spectra for a polycrystalline material known to have
1833   intergranular cracking were reported in [9]. The spectra were similar to those for two parallel
1834 R_pC_p elements in series although the experimental peaks were broader - they could be
1835   approximated as the sum of two Debye peaks of equal heights separated by about a decade in
1836   frequency, so that the maxima in Z'' and M'' could be approximated as $R_p / 4$ and $C_0/4C_p$,
1837   respectively. Computed values of R and C for the intergranular and granular material in the
1838   cracked sample, using these approximations and assuming a resolution into symmetric ρ'' peaks,
1839   were:

1840

1841   *Lower Frequency (Intergranular) Relaxation in Cracked Sample*

1842 $\tau_i = \dfrac{1}{\omega_{\max(Z'')}} = 6.4 \times 10^{-6} \text{ s}$,   (2.208)

1843 $R_i \approx 4Z''_{\max} = 6.4 \times 10^{6} \ \Omega$,   (2.209)

1844 $C_i = \dfrac{\tau_i}{R_i} \approx 1.0 \, \text{pF}$.   (2.210)

1845

1846   *Higher frequency (Intragranular) Relaxation in Cracked Sample*

1847 $\tau_c = \dfrac{1}{\omega_{\max(Z'')}} = 1.6 \times 10^{-7} \text{ s}$,   (2.211)

1848 $R_c \approx 4Z''_{\max} = 2.6 \times 10^{6} \ \Omega$,   (2.212)

1849 $C_c = \dfrac{\tau_c}{R_c} \approx 0.06 \, \text{pF}$ (2.213)

1850

1851   The impedance spectrum was drastically altered after the intergranular cracking had been
1852   annealed out [9]. A single peak in Z'' was observed in the annealed sample that was essentially
1853   indistinguishable from the high frequency peak in the cracked material, strongly suggesting that it
1854   was due to intra-crystal relaxation and that the additional low frequency peak for the cracked
1855   sample was due to thin air gaps. Consistent with this, the modulus spectrum was essentially
1856   unchanged by annealing since it was unaffected by the high capacitance cracks. The estimates of
1857   the intragranular and intergranular resistances were confirmed by the σ_0 data: the observed
1858   conductivity of the cracked sample was largely determined by the intergranular resistance, and the
1859   ratio of the conductivities of the sample before and after annealing should have been

1860

1861 $\dfrac{Z''^{low\omega}_{\max} + Z''^{high\omega}_{\max}}{Z''^{high\omega}_{\max}} = \dfrac{2.25 \times 10^{6}}{0.65 \times 10^{6}} = 3.5$,   (2.214)

1862

1863   in fair agreement with

1864

1865
$$\frac{\sigma_{annealed}}{\sigma_{cracked}} = 3.1.$$
(2.215)

1866
1867   The combination of modulus and impedance spectroscopies once again revealed details that could
1868   not be obtained from the original σ' and ε' data.
1869
1870   2.4.5.7 Intergranular Gas Adsorption
1871   The effects of oxygen and alkali doping on the electrical response of polycrystalline zinc
1872   oxide were studied by Seitz and Sokoly [71]. Only the effects of oxygen pressure are discussed
1873   here. An increase in conductivity was observed with decreasing oxygen pressure and the absence
1874   of changes due to different electrode materials implied that adsorbed oxygen at grain surfaces was
1875   responsible for the observed polarization of the sample. The conductivity and permittivity were
1876   plotted explicitly as a function of frequency and these data allowed M'' and ρ'' spectra to be
1877   calculated without difficulty (unpublished results obtained by the present author). The calculated
1878 M'' and ρ'' spectra exhibited two partially resolved peaks whose estimated magnitudes were
1879   consistent with a thin high capacitance - high resistance layer determining the low frequency
1880   response. Both peaks in the M'' spectrum had comparable half widths (ca. 1.5 decades) and their
1881   relative maximum values 8×10^{-4} and 1.1×10^{-2} (ratio 14) were a good (inverse) measure of the
1882   relative capacitance of each relaxation: $C_1 / C_h \approx 13$. The resistance ratio R_1 / R_h of the low
1883   frequency high frequency relaxation could then be estimated from the two values of f_{max} (ca.
1884 5×10^{2} and $3\times10^{5}\,\mathrm{Hz}$) to be about 45:
1885
1886
$$\frac{R_1 C_1}{R_h C_h} \approx 600 \approx \frac{13 R_1}{R_h} \Rightarrow \frac{R_1}{R_h} \approx 45.$$
(2.216)

1887
1888   The conductivity estimated from the height of the lower frequency resistivity peak was 1.1×10^{-7}
1889   S m^{-1}, in reasonable agreement with the low frequency plateau value of 1.3×10^{-7} S/m. From the
1890   relative frequencies of the M'' maxima and the relative heights of the (partly resolved) ρ'' maxima,
1891   the conductivity of the high frequency relaxation was estimated to be about $10^{-6\pm1}$ S m^{-1}. Because
1892   of its higher associated capacitance the lower frequency relaxation almost certainly corresponded
1893   to an intergranular impedance, and its removal by a reduction in oxygen pressure should therefore
1894   have increased the sample conductivity by about 45 but have a small effect on the measured
1895   permittivity (since removal of a high series capacitance has little effect on the total impedance).
1896   This predicted change in resistivity agreed with the qualitative statement that conductivity
1897   increased with decreasing oxygen pressure [71].
1898

1899

1900   Appendices

1901

1902   Appendix 2.1 Derivation of *M** for a Debye Relaxation with No Additional Separate
1903   Conductivity
1904   These derivations are shown for pedagogical clarity rather than mathematical elegance.

1905   (1) $\Delta\varepsilon \equiv \varepsilon_0^E - \varepsilon_\infty^E; \tau_D = \left(\varepsilon_\infty^E / \varepsilon_0^E\right)\tau_E; M_0^E = 1/\varepsilon_0^E; M_\infty^E = 1/\varepsilon_\infty^E$

1906   (2) $M^* = 1/\varepsilon^* \Rightarrow M' = \dfrac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}; M'' = \dfrac{-\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$

1907   (3) $\varepsilon' = \varepsilon_\infty^E + \dfrac{\left(\varepsilon_0^E - \varepsilon_\infty^E\right)}{1+\omega^2\tau_E^2} = \varepsilon_\infty^E + \dfrac{\Delta\varepsilon}{1+\omega^2\tau_E^2}; \varepsilon'' = \dfrac{\Delta\varepsilon\omega\tau_E}{1+\omega^2\tau_E^2}$

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

1908

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

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

1909   (4) $= \dfrac{1}{\varepsilon_0^E} + \dfrac{\varepsilon_\infty^E\omega^2\tau_E^2 - \dfrac{\varepsilon_\infty^2}{\varepsilon_0}\omega^2\tau_E^2}{\left(\varepsilon_0^E\right)^2\left(1+\dfrac{\left(\varepsilon_\infty^E\right)^2}{\left(\varepsilon_0^E\right)^2}\omega^2\tau_E^2\right)} = \dfrac{1}{\varepsilon_0^E} + \dfrac{\dfrac{\varepsilon_\infty^E}{\left(\varepsilon_0^E\right)^2}\omega^2\tau_E^2 - \dfrac{\left(\varepsilon_\infty^E\right)^2}{\left(\varepsilon_0^E\right)^3}\omega^2\tau_E^2}{\left(1+\dfrac{\left(\varepsilon_\infty^E\right)^2}{\left(\varepsilon_0^E\right)^2}\omega^2\tau_E^2\right)} = \dfrac{1}{\varepsilon_0^E} + \dfrac{\left(\dfrac{1}{\varepsilon_\infty^E}-\dfrac{1}{\varepsilon_0^E}\right)\dfrac{\left(\varepsilon_\infty^E\right)^2}{\left(\varepsilon_0^E\right)^2}\omega^2\tau_E^2}{\left(1+\dfrac{\left(\varepsilon_\infty^E\right)^2}{\left(\varepsilon_0^E\right)^2}\omega^2\tau_E^2\right)}$

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

1910

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

1911　　　(5)

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

1912
1913　　A Matlab®/Octave program for computing the components of *M** with added conductivity is
1914　　given below in Appendix 2.2.
1915

1916
1917   Appendix 2.2 Matlab®/GNU Octave Codes
1918   Computation Code for a Debye Relaxation with Additional Separate Conductivity σ_0.
1919   The   algebraic   derivation   is   excessively   tedious   and   is   replaced   here   by   a
1920   Matlab®/GNUOctave code that plots both components of the ε^* and M^* functions. The values
1921   of the input parameters are entered by editing the m-file.
1922
1923   % FUNCTION DebyeCondM Computes and Plots M* for Debye E* plus constant conductivity
1924   function HD = DebyeCondM
1925   w = logspace(-6,+6,1200);
1926   Logw = log10(w);
1927   E00   = 8.854E-12;   % Vacuum permittivity in F/m
1928   E0D   = 20;   % Low f dielectric relative permittivity
1929   EinfD = 10;   % High f dielectric relative permittivity
1930   DelE = E0D - EinfD;   % Dielectric dispersion range
1931   EinfE = 3;   % High f conductivity relative permittivity
1932   TauD = 10^-4   % Dielectric relaxation time
1933   Sigma0 = 10^-15;   % Conductivity in S/m
1934   Tausig = E00*EinfE/Sigma0   % Conductivity relaxation time
1935   E2sig = Sigma0./(E00*w);   % Conductivity contribution to E2
1936   % CALCULATE E1 and E2
1937   wTauD = w*TauD;
1938   Num = 1./(1 + wTauD.^2);
1939   E1 = EinfD + DelE*Num;   %Debye E1
1940   E2 = DelE*wTauD.*Num + E2sig; % Debye E2 + Conductivity E2
1941   Denom = E1.^2 + E2.^2;
1942   M1 = E1./Denom;
1943   M2 = E2./Denom;
1944   subplot (2,2,1);
1945   plot (Logw, E1);
1946   ylabel("E1");
1947   subplot (2,2,2);
1948   plot (Logw, E2);
1949   ylabel("E2");
1950   subplot (2,2,3);
1951   plot (Logw, M1);
1952   ylabel("M1");
1953   subplot (2,2,4);
1954   plot (Logw, M2);
1955   ylabel("M2");
1956
1957   return
1958

1959

1960   Appendix 2.3 Derivation of Debye Dielectric Expression from Equivalent Circuit

1961   Impedance of $R_s + C_s$ is

1962 $$Z_s = R_s + 1/i\omega C_s = (1 + i\omega R_s C_s)/i\omega C_s = (1 + i\omega \tau_s)/i\omega C_s \tag{C1}$$

1963   and its admittance is

1964 $$A_s = 1/Z_s = i\omega C_s /(1 + i\omega \tau_s) \tag{C2}$$

1965   where $\tau_s \equiv R_s C_s$. The total admittance is

1966 $$A^* = i\omega C_s /(1 + i\omega \tau_s) + G_p + 1/(i\omega C_p) \tag{C3}$$

1967   and the complex capacitance is

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

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

1968
$$= \frac{[C_p(1 + \omega^2 \tau_s^2) + C_s(1 - i\omega \tau_s)]}{1 + \omega^2 \tau_s^2} - \frac{iG_p}{\omega} \tag{C4}$$

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

1969   from which eqs. (2.154) and (2.155) obtain.

1970

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