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2   CHAPTER TWO: ELECTRICAL RELAXATION
3   1/29/2018
4   [FINAL DRAFT]

5 Contents

65

66

67 Preliminaries

68   The examples used to illustrate different applications are not central to the purpose of this
69 book and are not recent. Some of the applications have been discussed in an unpublished but
70 widely circulated paper by the present author that is reproduced in Appendix A (original errors
71 have been corrected and the conversion to the phase convention used by everyone except
72 electrical engineers has been made.)

73

74 2.1   Nomenclature
75 Italicized lower case letters are used for physical variables, e.g. {x, y, z, r} for distances, t for
76 time, and q for charge; italicized upper case letters are used for specific values of variables and
77 field magnitudes, e.g. {X, Y, Z, R}, T, Q. Vectors are denoted by bold face upper case letters with
78 an arrow $\vec{\mathbf{V}}$ and tensors are denoted by bold face upper case $\mathbf{T}$.

79   There are two time constants for relaxation of polarization, one for relaxation at constant

80 electric field (i.e. dielectric relaxation of the displacement $\vec{\mathbf{D}}$) denoted by τ_E and one for

81 relaxation at constant displacement (i.e. conductivity relaxation of the electric field $\vec{\mathbf{E}}$) denoted

82 by τ_D. Amongst other things these two distinct time constants correspond to two microscopic
83 time constants for a single macroscopic dielectric time constant, as has been briefly discussed in
84 ref. [1].

85   Dielectric and conductivity relaxations can both occur in the same material over two
86 resolvable frequency ranges and the usual nomenclature for the low and high frequency limits of a
87 single relaxation process (e.g. ε_0 and ε_∞ for the relative permittivity) is ambiguous and has
88 caused confusion in a long standing debate about the legitimacy of the electric modulus
89 formalism. We introduce a new nomenclature here to distinguish the low and high frequency
90 limits for the two possible relaxations that, although somewhat clumsy, eliminates this confusion.

91 The two limits for a dielectric relaxation at constant $\vec{\mathbf{E}}$ are denoted by ε_0^E and ε_∞^E and the two

92 limits for a conductivity relaxation at constant $\vec{\mathbf{D}}$ are denoted by ε_0^D and ε_∞^D. Since a
93 conductivity relaxation must in general occur at lower frequencies than a dielectric relaxation for
94 the latter to be readily observed (with some exceptions depending on instrumental sensitivity)
95 then $\varepsilon_\infty^D = \varepsilon_0^E$, although overlap can occur.

96   Electric charge is denoted by q (Coulomb C), volume charge density by ρ $\left(\mathrm{C\,m^{-3}}\right)$,

97 surface charge density by σ $\mathrm{C\,m^{-2}}$, linear charge density by λ $\mathrm{C\,m^{-1}}$, current by I (Ampere = A =

98 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

99 $\left(\mathrm{N\,C^{-1}} = \mathrm{V\,m^{-1}}\right)$, electric dipole moment by μ_E (C.m), resistance by R (Ohm = $\Omega = \mathrm{V\,A^{-1}}$), and

100 capacitance by C (Farad F = $\mathrm{C\,V^{-1}}$). The SI unit for conductance (=1/resistance) is the Siemen S
101 (equal to Ω^{-1}).

102

103   2.2   Electromagnetism
104   2.2.1   Units
105   Two systems of electromagnetic units are in use, the cgs (centimeter-gram-second) and the
106   MKS (meter-kilogram-second) or SI (Systeme Internationale). The SI system is the official
107   scientific system but the cgs system appears in older publications and since it is still used by
108   chemists and materials scientists its relationship to the SI system is delineated here. For
109   mechanics only the numerical value of physical quantities changes with the system of units, but in
110   electromagnetism there is an additional difference of approach: electric charge in the cgs system
111   is defined in the fundamental units mass-length-time whereas in the SI it is defined to be just as
112   fundamental as mass, length and time: this SI unit of charge is the Coulomb.
113   The cgs form of Coulomb's law for the force F between two point charges q_1 and q_2
114   separated by a distance r and immersed in a medium of (dimensionless) permittivity ε is
115

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

117

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

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

123

124   that gives dimensions of $M^{1/2} L^{1/2}$ for the electromagnetic unit (emu) of charge. The esu and emu
125   units differ by a factor LT^{-1} that has the dimensions of speed and the value of the speed of light,
126   c. This is the reason that c enters into many cgs formulae. Numerically, $\text{emu} = c\,\text{esu}$ (c in cgs
127   units = 2.9979×10^{10} cm/s).
128   The Coulomb C is defined experimentally by its time derivative, the current in amperes A,
129   that in turn is determined using eq. (2.2). A constant μ_0 is inserted into the SI form for this
130   magnetic force to ensure consistency with the cgs system: the same force is produced by the same
131   currents separated by the same distance
132

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

134

135   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
136   Law [eq. (1.150) and eq. (2.19) below] and is a frequent source of confusion. The SI form of
137   Coulomb's law is
138

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

140

141 where e_0 is a constant (the permittivity of free space), with dimensions $Q^2 M^{-1} L^{-3} T^2$ that
142 correspond to the units of capacitance per unit length (Farads meter^{-1}). Comparing eqs. (2.1) and
143 (2.4) reveals that
144
145 $(\text{esu})^2 = 4\pi e_0 (\text{Coulomb})^2$. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (2.5)
146
147 The algebraic conversion between cgs and SI units for charge also needs to account for the ratio
148 of the different units for force (10^5). The eventual numerical relations between C, esu and emu are
149 $C \approx 3 \times 10^9 \text{esu} \approx 10^{-1} \text{emu}$, where the approximate equality arises from placing the speed of light
150 at 3×10^8 m^{-1} rather than $2.9979... \times 10^8$ m^{-1}. The dimensionless fine structure constant α in cgs
151 units is $\alpha = e^2 / \hbar c = 2\pi e^2 / hc$ (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
152 Coulomb). It is easily confirmed that the SI value of α is dimensionless and has the same
153 numerical value as the cgs value.
154 $\qquad$ Having illustrated the cgs system to this point it is now dispensed with apart from one
155 occasional exception: the unit for the molecular dipole moment. In the SI system this is the
156 coulomb-meter but this unit is inconveniently large and is rarely (ever?) used. The more common
157 unit is the Debye, defined as the dipole moment created by two opposite charges of 10^{-10} esu
158 $(3.3 \times 10^{-20} \text{ C})$ separated by 1.0 Angstrom (10^{-10} m). The persistence of this unit probably
159 originates in the fact that molecular dipole moments are of order unity when expressed in Debyes
160 (D) but of order 10^{-30} in coulomb-meters. It is not clear to this author why a convenient SI unit
161 such as 10^{-31} C.m ≈ 0.33 D or 10^{-30} C.m ≈ 3.3 D has not been introduced, especially since the
162 SI unit nm has replaced the Angstrom in optical spectroscopy. Perhaps indecision by the
163 international committee about who to name the unit after? What about Onsager (O) for example?
164
165 2.2.2 Electromagnetic Quantities
166 $\qquad$ Many of these are conveniently defined using a parallel plate capacitor comprising two
167 conducting flat plates, each of area A and separated by a distance d. The geometric "cell constant"
168 k is
169
170 $k \equiv d / A$. $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (2.6)
171
172 Each plate has a charge of magnitude q_0 but of opposite sign (uniformly distributed since the
173 plates are conducting) that produces an electric potential difference V between the plates. The
174 capacitance is $C \equiv q_0 / V$ that has the units unit Farad = C V^{-1}. The surface charge density
175 $\sigma_0 = \pm q_0 / A$ on the plates induces an interfacial charge density $\mp \sigma_i$ on each surface of any
176 dielectric material between the plates. The electric field $\vec{E}$, polarization $\vec{P}$ and displacement
177 vector $\vec{D}$ are perpendicular to the plates with magnitudes defined by the following table:
178

SI	cgs	
$D = \sigma_0$	$D = 4\pi\sigma_0$	(2.7)
$P = \sigma_i$	$P = \sigma_i$	(2.8)
$e_0 E = \sigma_0 - \sigma_i = D - P$	$E = 4\pi(\sigma_0 - \sigma_i) = D - 4\pi P$	(2.9)

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

$$\vec{\mathbf{D}} = \nabla\rho \tag{2.10}$$

and

$$\vec{\mathbf{E}} = \nabla\varphi_E . \tag{2.11}$$

The inverse of eq. (2.11) is

$$\varphi_{1,2} = \int_{s_1}^{s_2} \vec{\mathbf{E}} \cdot d\vec{\mathbf{s}} \tag{2.12}$$

where $\varphi_{1,2}$ is the potential difference between the points s_1 and s_2. The relative permittivity ε and dielectric susceptibility χ_d are defined in the following table:

SI	cgs	
$\varepsilon \equiv \dfrac{D}{e_0 E}$	$\varepsilon \equiv \dfrac{D}{E}$	(2.13)
$\chi_d = \dfrac{P}{e_0 E} = \dfrac{D - e_0 E}{e_0 E} = \varepsilon - 1$	$\chi_d = \dfrac{P}{E} = \dfrac{D - E}{4\pi E} = \dfrac{1}{4\pi}(\varepsilon - 1)$	(2.14)

A dielectric material between the plates decreases the electric field between the plates because the induced polarization charge density σ_i on the surface of the material partly cancels the unchanged charge density on the plates [eq. (2.9)]. The units of D and P (charge area^{-1}) correspond to dipole moment (charge-distance) per unit volume. In view of $\vec{\mathbf{D}}$, $\vec{\mathbf{E}}$ and $\vec{\mathbf{P}}$ being vectors the relative permittivity and dielectric susceptibility are in general tensors but for isotropic media (liquids, glasses, and isotropic crystals) D, E, P and ε are all scalars. We mostly treat them as scalars in this book.

The magnetic analogs of D, E, P, e_0, ε and χ_d are, respectively, the magnetic induction B, the magnetic field H, the magnetization M, the permeability of free space, μ_0, the relative permeability μ, and the magnetic susceptibility χ_m. The SI and cgs definitions are

214
215

SI	cgs	
$B = \mu_0 H$	$B = H$	(2.15)

217 $M = \dfrac{B}{\mu_0} - H$ $M = \dfrac{B - H}{4\pi}$ (2.16)

218 $\mu = \dfrac{B}{H}$ $\mu = \dfrac{B}{H}$ (2.17)

219 $\chi_M = \dfrac{M}{H} = \dfrac{B}{\mu_0 H} - 1$ $\chi_M = \dfrac{M}{H} = \dfrac{B}{4\pi H} - 1$ (2.18)

220
221 2.2.3 Electrostatics
222   Gauss's Law is
223

224 $\displaystyle\oint_S \mathrm{e}_0 \varepsilon \vec{\mathbf{E}} \bullet d\vec{\mathbf{A}} = q_{enclosed} \Rightarrow \oint_S \vec{\mathbf{D}} \bullet d\vec{\mathbf{A}} = q_{free}$,   (2.19)

225
226 where $q_{enclosed}$ is the total net charge within a closed surface S of magnitude A, ε is the relative
227 permittivity of the material enclosed by the surface, and the surface integral is the flux of the
228 electric field through the surface. For the definition in terms of $\vec{\mathbf{D}}$ the quantity q_{free} does not
229 include the induced polarization charges because these are subsumed into the permittivity $\mathrm{e}_0 \varepsilon$.
230 Equation (2.19) is the electrical version of the mathematical Gauss's Theorem in Chapter One [eq.
231 1.146)]. As noted in Chapter One the differential area vector $d\vec{\mathbf{A}}$ of a surface is defined as having
232 a direction perpendicular to the plane of the surface, and for closed surfaces such as occur in
233 Gauss's Law the outward pointing direction is defined to be positive. The Gaussian surface is a
234 purely mathematical object that can be placed anywhere although it must have the same symmetry
235 as the system under study to be helpful. Thus information about charge distribution can be
236 inferred even though E is determined by the total enclosed charge.
237   Gauss's Law is now used to calculate $\vec{\mathbf{E}}$ and the capacitance C for several geometries and
238 charge distributions. The geometrical objects and charges are taken to be immersed in a medium
239 of relative permittivity ε.
240
241 2.2.3.1 Point Charge (Coulomb's Law)
242   Define the Gaussian surface S as a sphere of radius r with a point charge q at its center. By
243 symmetry $\vec{\mathbf{E}}$ is everywhere parallel to $d\vec{\mathbf{a}}$ and has a constant magnitude E obtained from
244 $q = \mathrm{e}_0 \varepsilon \oint \vec{\mathbf{E}} \cdot d\vec{\mathbf{A}} = 4\pi r^2 \mathrm{e}_0 \varepsilon E$ so that
245

246 $E = \dfrac{q}{4\pi \varepsilon \mathrm{e}_0 r^2}$.   (2.20)

247

248   2.2.3.2 Long Thin Rod with Uniform Linear Charge Density λ
249   Define the Gaussian surface to be a cylinder of radius r and length L, with the rod on its
250   central axis. Then $q = \varepsilon e_0 \oint_S \vec{\mathbf{E}} \bullet d\vec{\mathbf{A}} = \varepsilon e_0 E (2\pi r L)$ so that at a distance r from the axis

251

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

253

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

261   so that
262

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

264

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

266

267   2.2.3.4 Flat Conducting Plate
268   Let the charge on each side of the plate be q/2 and define the Gaussian surface to be the
269   same as that for the insulating plate in §2.2.3.3. The electrostatic field inside a conductor is zero
270   so   that   the   electric   field   points   away   each   surface   of   the   plate   and
271    $q/2 = \sigma A/2 = e_0 \varepsilon \oint_S \vec{\mathbf{E}} \bullet d\vec{\mathbf{A}} = e_0 \varepsilon EA$ so that

272

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

274

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

276

277   2.2.3.5 Two Parallel Insulating Flat Plates
278   Consider charges ±q that are uniformly distributed over both surfaces of the plate. The
279   field between the plates is the vector sum of the fields from each plate. Since the field from the
280   positively charged plate points away from the positive plate and the field from the negatively
281   charged plate points toward the negative plate the two fields add up and the electric field is twice
282   that of eq. (2.22):
283

284 $$E = \frac{\sigma}{\varepsilon e_0}.$$ (2.24)

285

286 **2.2.3.6 Two Parallel Conducting Flat Plates**

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

291

292 $$E = \frac{\sigma}{\varepsilon e_0}.$$ (2.25)

293

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

296   The capacitance is obtained from the voltage difference $V = E.d$ V between the plates and
297 $q = A\sigma_0$:

298

299 $$C = \frac{q}{V} = \frac{\sigma_0 A}{Ed} = \frac{\sigma_0 A/d}{e_0\varepsilon/\sigma_0} = (A/d)(e_0\varepsilon) = (e_0\varepsilon/k),$$ (2.26)

300

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

302

303 **2.2.3.7 Concentric Conducting Cylinders**

304   Define the inner and outer radii of two concentric conducting cylindrical plates to be a and
305 b, respectively, let their equal height be h, and let charges +q and −q be uniformly distributed on
306 the inside surfaces of each plate. Consider a concentric cylindrical Gaussian surface of radius
307 $a < r < b$ and height h, so that $q/e_0\varepsilon = \oint_S \vec{E} \cdot d\vec{A} = E(2\pi rh)$. Then

308

309 $$E = q/(2\pi rh e_0\varepsilon)$$ (2.27)

310

311 so that

312

313 $$V = \int_a^b E dr = \left(\frac{q}{2\pi h e_0\varepsilon}\right)\int_a^b \frac{dr}{r} = \frac{q}{2\pi h e_0\varepsilon}\ln\left(\frac{b}{a}\right)$$ (2.28)

314

315 and the capacitance is

316

317 $$C = \frac{q}{V} = \frac{2\pi h e_0\varepsilon}{\ln\left(b/a\right)}$$ (2.29)

318
319   2.2.3.8 Concentric Conducting Spheres
320   Define the inner and outer radii of two concentric spherical conducting plates to be a and
321   b, respectively, and let charges +q and –q reside on the inside surfaces of each plate. Consider a
322   concentric spherical Gaussian surface of radius $a < r < b$ so that $q/\mathrm{e}_0 = \oint_S \vec{E} \bullet d\vec{A} = E\left[4\pi r^2\right]$ and
323     $E = q/\left[4\mathrm{e}_0\pi r^2\right]$. Then
324

325     $$V = \int_a^b E dr = \frac{q}{4\pi\mathrm{e}_0\varepsilon}\int_a^b \frac{dr}{r^2} = \frac{q}{4\pi\mathrm{e}_0\varepsilon}\left(\frac{1}{b}-\frac{1}{a}\right) = \frac{q}{4\pi\mathrm{e}_0\varepsilon}\left(\frac{a-b}{ab}\right)$$ (2.30)

326
327   and

328     $$C = \frac{q}{V} = 4\pi\mathrm{e}_0\varepsilon\left(\frac{ab}{b-a}\right).$$ (2.31)

329
330   2.2.3.9 Isolated Sphere
331   The capacitance of an isolated sphere is obtained from eq. (2.31) by taking the limit
332     $b \rightarrow \infty$ and for convenience placing $a = R$:
333
334     $$C = 4\pi\mathrm{e}_0\varepsilon R.$$ (2.32)

335
336   Thus larger spheres have larger capacitances.
337
338   2.2.4   Electrodynamics
339   Consider a constant voltage V applied across two parallel plates between which there is
340   now a conducting medium. Let the resistivity of the material be $\rho = R.k^{-1}$ (units ohm-meter) and
341   specific conductivity $\sigma = 1/\rho$ (units S m⁻¹), where R is the resistance between the plates in ohms
342   and the symbol S refers to the SI unit Siemen defined as the reciprocal of the ohm. The current
343   density $\vec{J}$ is the electric current per unit area (units A m⁻²) so that $\vec{J}\rho = \vec{E}$. Unfortunately the
344   displacement current $dD/dt = d\sigma_0/dt$ (better named as the displacement current density) has no
345   symbol.
346   Electric current, symbol I, is defined as
347

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

349
350   so that the total charge that passes across a plane through which a current I flows is
351

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

353

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

357

358 $$R \equiv \frac{V}{I} \qquad (2.35)$$

359

360 and $\Omega = V / A$. An electrical conductor is said to be ohmic if, and only if, R is constant. This is
361 not the same as $dV / dI =$ constant: for example if $V = 1.0 + 2I$ so that $dV/dI = 2$ then
362 $R = 3\Omega$ for $I = 1\,\text{A}$, $R = 2.5\Omega$ for $I = 2\,\text{A}$, $R = 2.3\Omega$ for $I = 3\,\text{A}$.
363 　　　Resistances dissipate power P given by $P = IV$ (recall that energy is given by QV and
364 power is the time derivative of energy). For ohmic resistances
365

$$\begin{aligned}
P &= IV \\
&= I(IR) = I^2 R \\
&= (V/R)V = V^2/R.
\end{aligned} \qquad (2.36)$$

366

367
368 2.2.5　Maxwell's Equations
369 　　　These four equations summarize all that is known about electromagnetic phenomena –
370 they are essentially the electromagnetic equivalent of Newton's laws for mechanics but are more
371 mathematically sophisticated because of the greater complexity of electromagnetic phenomena.
372 　　　The differential forms of the four Maxwell equations are:

373

374 $\vec{\nabla}\bullet\vec{\mathbf{D}} = \rho$; $\qquad (2.37)$

375 $\vec{\nabla}\bullet\vec{\mathbf{B}} = 0$; $\qquad (2.38)$

376 $\vec{\nabla}\times\vec{\mathbf{E}} = -\left(\dfrac{\partial\vec{\mathbf{B}}}{\partial t}\right)$; $\qquad (2.39)$

377 $\vec{\nabla}\times\vec{\mathbf{H}} = \vec{\mathbf{J}} + \left(\dfrac{\partial\vec{\mathbf{D}}}{\partial t}\right)$ $\qquad (2.40)$

378 $\qquad = \sigma\vec{\mathbf{E}} + \left(\dfrac{\partial\vec{\mathbf{D}}}{\partial t}\right)$ $\qquad (2.41)$

379 $\qquad = \sigma\vec{\mathbf{E}} + \mathrm{e}_0\left(\dfrac{\partial\varepsilon\vec{\mathbf{E}}}{\partial t}\right)$. $\qquad (2.42)$

380
381 Equation (2.40) for a vacuum is equivalent to
382

383 $\vec{\nabla}\times\vec{\mathbf{B}} = \mu_0\vec{\mathbf{J}} + \mu_0\mathrm{e}_0\left(\dfrac{\partial\vec{\mathbf{E}}}{\partial t}\right)$, $\qquad (2.43)$

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

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

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

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

388   because the vector identity $\vec{\nabla}\bullet\left(\vec{\nabla}\times\vec{\mathbf{H}}\right)=0$ would then imply $\vec{\nabla}\bullet\vec{\mathbf{J}}=0$. The difficulty is resolved

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

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

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

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

393

394    $$\vec{\nabla}\bullet\left(\vec{\nabla}\times\vec{\mathbf{H}}\right)\equiv 0=\vec{\nabla}\left[\left(\frac{\partial q_0}{\partial t}\right)-\left(\frac{\partial q_i}{\partial t}\right)\right] \qquad (2.44)$$

395   is ensured.

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

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

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

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

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

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

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

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

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

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

406   magnetic field as migration of individual charges.

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

408

409    $$\vec{\nabla}\times\vec{\mathbf{A}}=\vec{\mathbf{B}} \qquad (2.45)$$

410

411   and

412

413    $$\vec{\mathbf{E}}=-\vec{\nabla}\varphi_E-\frac{\partial\vec{\mathbf{A}}}{\partial t}, \qquad (2.46)$$

414

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

416   ensures eq. (2.38) because of the vector identity $\vec{\nabla}\bullet\left(\vec{\nabla}\times\vec{\mathbf{A}}\right)=0$ and eqs. (2.45) and (2.46)

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

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

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

420   following consideration indicates: if $\partial \vec{\mathbf{B}} / \partial t \neq 0$ then $\vec{\nabla} \times \vec{\mathbf{E}} \neq 0$ by eq. (2.38) and the static
421   relation
422

423      $\vec{\mathbf{E}} = \vec{\nabla} \varphi_E$ (2.47)

424

425   could then never hold because of the vector identity $\vec{\nabla} \times \left(\vec{\nabla} \varphi_E \right) = 0$. But $\vec{\mathbf{E}}$ is known to be

426   nonzero in dynamic situations (hence currents). Similarly if $\vec{\mathbf{J}} \neq 0$ or $\partial \vec{\mathbf{D}} / \partial t \neq 0$ then there is

427   no potential φ_B for $\vec{\mathbf{B}}$ (defined by $\vec{\mathbf{B}} = \vec{\nabla} \varphi_B$) because eq. (2.40) then implies

428      $\vec{\nabla} \times \vec{\mathbf{H}} = \vec{\nabla} \times \vec{\mathbf{B}} / \mu \mu_0 \neq 0$ because of the same vector identity $\vec{\nabla} \times \left(\vec{\nabla} \varphi_B \right) = 0$. Both of these

429   difficulties are averted by the introduction of $\vec{\mathbf{A}}$. Equation (2.46) is then consistent with eq.
430   (2.39) since it guarantees
431

432      $\vec{\nabla} \times \vec{\mathbf{E}} = \vec{\nabla} \times \left(-\vec{\nabla} \varphi_E - \dfrac{\partial \vec{\mathbf{A}}}{\partial t} \right) = -\dfrac{\partial \vec{\mathbf{B}}}{\partial t}$.   (2.48)

433
434   Integral versions of Maxwell's equations include Faraday's Law:
435

436      $\oint \vec{\mathbf{E}} \bullet d\vec{\mathbf{s}} = -\dfrac{d\Phi_B}{dt}$; $\Phi_B \equiv \oint \vec{\mathbf{B}} \bullet d\vec{\mathbf{A}} = \text{magnetic flux}$ (2.49)

437
438   and Ampere's law
439

440      $\oint \vec{\mathbf{B}} \bullet d\vec{\mathbf{s}} = \mu_0 e_0 \dfrac{d\Phi_E}{dt} + \mu_0 I_{enclosed}$; $\Phi_E \equiv \oint \vec{\mathbf{E}} \bullet d\vec{\mathbf{A}} = \text{electric flux}$.   (2.50)

441
442   Equation (2.42) provides a convenient demonstration of the equivalence of the complex
443   permittivity and complex conductivity. First convert eq. (2.42) from a vector equation to a
444   complex scalar equation:
445

446      $\vec{\nabla} \times \vec{\mathbf{H}} = \sigma \vec{\mathbf{E}} + e_0 \left(\dfrac{\partial \varepsilon \vec{\mathbf{E}}}{\partial t} \right) \Rightarrow \left| \vec{\nabla} \times \vec{\mathbf{H}} \right| = \sigma^* E^* + e_0 \varepsilon^* \left(\dfrac{\partial E^*}{\partial t} \right)$.   (2.51)

447
448   For a sinusoidal excitation $E^* = E_0 \exp\left(-i\omega t \right)$ eq. (2.51) becomes
449

450      $\begin{aligned} \left| \vec{\nabla} \times \vec{\mathbf{H}} \right| &= \sigma^* E_0 \exp\left(-i\omega t \right) - e_0 \varepsilon^* E_0 \left(i\omega \right) \exp\left(-i\omega t \right) \\ &= \left[\sigma^* - i\omega e_0 \varepsilon^* \right] E_0 \exp\left(-i\omega t \right) \\ &= \left[\varepsilon^* - \sigma^* / \left(i\omega e_0 \right) \right] \left(-i e_0 \omega \right) E_0 \exp\left(-i\omega t \right), \end{aligned}$ (2.52)

451

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

453 $[\varepsilon*-\sigma*/(i\omega e_0)]$ provide equivalent descriptions of electrical relaxation, as do the resistivity

454 $\rho*=1/\sigma*$ and electric modulus $M*=1/\varepsilon*$. All these different functions emphasize or suppress

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

456 eq. (2.106) below].

457

458 2.2.6 Electromagnetic Waves

459 The Maxwell equations together with the constitutive relations $\vec{D}=e_0\varepsilon\vec{E}$ and $\vec{B}=\mu_0\mu\vec{H}$

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

461

462
$$\frac{c}{n}=\frac{(1/e_0\mu_0)^{1/2}}{(\varepsilon\mu)^{1/2}}=\frac{1}{(e_0\varepsilon\mu_0\mu)^{1/2}},\tag{2.53}$$

463

464 where

465

466
$$n=(\varepsilon\mu)^{1/2}\tag{2.54}$$

467

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

469

470
$$(n*)^2=(n'-in")^2=(n'^2-n"^2)-2in'n"=\varepsilon*=\varepsilon'-i\varepsilon"\tag{2.55}$$

471

472 so that

473

474
$$\varepsilon'=n'^2-n"^2\tag{2.56}$$

475

476 and

477

478
$$\varepsilon"=2n'n".\tag{2.57}$$

479

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

481 complex, $\mu*=\mu'-i\mu"$,

482

483
$$(n*)^2=(n'^2-n"^2)-2in'n"=(\varepsilon'-i\varepsilon")(\mu'-i\mu")\tag{2.58}$$

484

485 so that

486

487
$$(n*)^2=(n'^2-n"^2)-2in'n"=(\varepsilon'-i\varepsilon")(\mu'-i\mu")=(\varepsilon'\mu'-\varepsilon"\mu")-i(\varepsilon'\mu"+\varepsilon"\mu'),\tag{2.59}$$

488

489 and

490

491 $$n'' = \left(\varepsilon' \mu'' + \varepsilon'' \mu' \right).$$ (2.60)

492

493 Thus absorption of electromagnetic energy by magnetically lossy materials is enhanced by a high
494 relative permittivity and dielectric loss is enhanced in magnetic materials.

495   The electric field component of a plane electromagnetic traveling wave of angular
496 frequency ω propagating in the +x direction in a medium with refractive index n and speed c/n is

497 $$E(x,t) = E_0 \exp\left\{ -i\omega\left[t - \frac{nx}{c} \right] \right\},$$ (2.61)

498

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

500

501
$$E(x,t) = E_0 \exp\left\{ -i\omega\left[t - \frac{(n'-n'')x}{c} \right] \right\}$$
$$= E_0 \exp\left\{ -i\omega\left[t - \frac{n'x}{c} \right] \right\} \exp\left[\frac{-n''\omega x}{c} \right],$$ (2.62)

502

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

505

506
$$I = E_0^2 \exp\left\{ -2i\omega\left[t - \frac{(n'-in'')x}{c} \right] \right\}$$
$$= E_0 \exp\left\{ -2i\omega\left[t - \frac{n'x}{c} \right] \right\} \exp\left[\frac{-2n''\omega x}{c} \right],$$ (2.63)

507

508 that is to be compared with Beer's Law

509

510 $$I = I_0 \exp(-\alpha x),$$ (2.64)

511

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

515

516 $$\alpha(\omega) = \frac{2\omega n''(\omega)}{c}.$$ (2.65)

517

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

520 $E(x,t) = E_0 \exp\{+i\omega[t - nx/c]\}$ and the sign of the imaginary component of ε^* remained
521 negative then α would have to be negative and Beer's Law would predict unphysical exponential
522 growth through a medium. This can be resolved by making the imaginary component of ε^*
523 positive but this corresponds to a dipole rotation that leads the excitation voltage rather than lags
524 it. Nonetheless this is the convention used by electrical engineers and is the price paid for the
525 "advantage" of having a positive sign in the complex exponential. An excellent account of phase
526 conventions is given in Chapter One of ref. [2].
527   Insertion of eq. (2.57) into eq. (2.65) yields
528

529 $$\alpha(\omega) = \frac{\omega \varepsilon''(\omega)}{n'(\omega)c},$$ (2.66)

530

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

532

533 $$\alpha(\omega) = \frac{\sigma'(\omega)}{n'(\omega)e_0 c}.$$ (2.67)

534

535 Thus $n'', \varepsilon'', \alpha$ and σ' are all measures of absorption of electrical energy:

536

537 $$\alpha = \frac{\sigma'}{n e_0 c} = \frac{\omega \varepsilon''}{nc} = \frac{2\omega n''}{c}.$$ (2.68)

538

539   Ordinary em radiation comprises randomly distributed directions of polarization for the $\vec{\mathbf{E}}$
540 and $\vec{\mathbf{B}}$ fields (that are always perpendicular to one another). Radiation for which the direction of
541 polarization is constant and the same for all waves is said to be polarized. Reflected em waves are
542 partially polarized in the direction parallel to the reflecting surface, the extent of polarization
543 depending on the angle of incidence. Polaroid® sun glasses are polarized in the vertical direction
544 and therefore more strongly attenuate reflected waves. Reflected em waves are fully polarized at
545 the Brewster incident angle.

546

547 2.2.7   Local Electric Fields
548   The electric field inside a dielectric medium is not equal to the applied field because of
549 electrostatic screening by the medium. This is a complicated problem that is well described in
550 Chapter One of ref. [3] (by N. E. Hill) and has been considered by Onsager [4], Kirkwood [5],
551 and Frohlich [6]. The complexity of the issue is illustrated by the Kirkwood relation between the
552 isolated molecular dipole moment μ_g observed in the gas phase and the relative permittivity ε_0^E

553

554 $$\frac{4\pi N g \mu_g^2}{9 k_B T V e_0} = \frac{\left(\varepsilon_0^E - \varepsilon_\infty^E\right)\left(2\varepsilon_0^E + \varepsilon_\infty^E\right)}{\varepsilon_0^E\left(\varepsilon_\infty^E + 2\right)},$$ (2.69)

555

556   where ε_∞^E is the limiting high frequency relative permittivity that for a pure dielectric equals the
557   square of the (limiting low frequency) refractive index n^2, N is the number of dipoles in a volume
558   V, and g is a correlation factor that corrects for nonrandom orientations of surrounding dipoles
559   caused by direction dependent intermolecular forces. The latter is in principle calculable:
560

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

562

563   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
564   computed for specific orientation geometries.
565   The treatment of local field effects on the kinetics of dipole relaxation is even more
566   intricate because the reaction field produced by polarization of the dielectric medium by the
567   embedded dipole is in general out of phase with the applied field. These effects have been
568   discussed by Mountain [7]. A particularly important effect of local fields on relaxation
569   phenomenology is that a single macroscopic dielectric relaxation time corresponds to two
570   microscopic times. After a heated debate in the literature the accepted microscopic dipole
571   correlation function is the Fatuzzo and Mason [8] expression
572

573
$$\varphi(t) = \left(1 + \frac{\varepsilon_\infty}{2\varepsilon_0}\right)^{-1}\left[\exp\left(-\frac{t}{\tau_E}\right) + \left(\frac{\varepsilon_\infty}{2\varepsilon_0}\right)\exp\left(-\frac{\varepsilon_0}{\varepsilon_\infty}\frac{t}{\tau_E}\right)\right]$$
$$= \left(1 + \frac{\varepsilon_\infty}{2\varepsilon_0}\right)^{-1}\left[\exp\left(-\frac{t}{\tau_E}\right) + \left(\frac{\varepsilon_\infty}{2\varepsilon_0}\right)\exp\left(-\frac{t}{\tau_D}\right)\right], \tag{2.71}$$

574

575   where τ_E and τ_D are again the relaxation times for polarization at constant E and D respectively.
576   Fulton [9] has given a detailed discussion of this subject in which he deduced that the longitudinal
577   part of polarization relaxes with a time constant τ_D and that the transverse component relaxes

578   with a time constant τ_E. Electrical relaxation is therefore discussed later in this chapter in two
579   parts - dielectric relaxation and conductivity relaxation.
580

581   2.2.8   Circuits
582   There are the four fundamental elements in analog passive circuits: resistance R;
583   capacitance C; self inductance L; mutual inductance M.
584

585   2.2.8.1 Simple Circuits
586   Resistances in Series and in Parallel
587   For resistances R_i connected in series the same current I must pass through each and the
588   sum of the voltages across each resistor equals the applied voltage. Thus $V = \sum V_i = I \sum R_i = IR_s$
589   and the equivalent series resistance R_s is
590

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

592

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

596

597    $1/R_p = \sum 1/R_i$.   (2.73)

598

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

605

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

607

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

612

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

614

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

619

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

621

622   and since admittances add in parallel the equivalent parallel inductance I_p is

623

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

625

626　　　　　For the sake of completion the mutual inductance M is now described although for reasons
627　given below it rarely comes into play for relaxation phenomena or insrumentation. It is defined as
628　$M = V_2 / (dI_1 / dt)$, where V_2 is the voltage induced on one side of the device by a time varying
629　current I_1 in the other. Rearrangement of this definition of M yields
630
631　$V_2 = M (dI_1 / dt),$　　　　　　　　　　　　　　　　　　　　　　　　　　(2.78)
632
633　so that V_2 is smaller at lower frequencies when dI_1/dt is smaller. This is why transformer arm (ac
634　Wheatstone) bridges are useless at low frequencies. Series and parallel combinations of mutual
635　inductances add up in the same way as self inductances.
636
637　Combined Series and Parallel Elements
638　　　　　Consider two examples of a circuit in which an element Z_1 is in parallel with a series
639　combination of two elements Z_2 and Z_3. If these elements are resistances R_1, R_2 and R_3 then
640　$R_{23} = R_2 + R_3$ and
641
642　$$\frac{1}{R_{equiv}} = \frac{1}{R_1} + \frac{1}{R_2 + R_3} = \frac{R_1 + R_2 + R_3}{R_1 (R_2 + R_3)}$$　　　　　　　　　　(2.79)
643
644　or
645
646　$$R_{equiv} = \frac{R_1 (R_2 + R_3)}{R_1 + R_2 + R_3}.$$　　　　　　　　　　　　　　　　　　　(2.80)
647
648　　　　　If　　these　　elements　　are　　capacitances　　C_1,　　C_2　　and　　C_3　　then
649　$1/C_{23} = 1/C_2 + 1/C_3 \Rightarrow C_{23} = C_2 C_3 / (C_2 + C_3)$ and
650
651　$$C_{equiv} = C_1 + C_{23} = C_1 + \frac{C_2 C_3}{C_2 + C_3} = \frac{C_1 C_2 + C_2 C_3 + C_3 C_1}{C_2 + C_3}.$$　　　　(2.81)
652
653　2.2.8.2 AC Circuits
654　　　　　If a voltage $V(t) = V_0 \cos(\omega t) = \text{Re}[V_0 \exp(-i\omega t)]$ is applied across a circuit the average
655　voltage over one period is zero but the ac power is not. Equation (2.36) indicates that power is
656　determined by the averages of I^2 and V^2 that are both proportional to the averages of $\sin^2(\omega t)$ or
657　$\cos^2(\omega t)$ over one cycle that are both equal to $\frac{1}{2}$. Thus
658
659　$P_{average} = (V_0^2 / 2) R = I_0^2 R / 2.$　　　　　　　　　　　　　　　　　　(2.82)
660
661　The ac power dissipation is therefore given by the same relation for DC power dissipation if the

662   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
663   latter are referred to as rms (root mean square) voltages and currents. Electrical outlet ac voltages
664   such as 120V in North America are given as rms values; the peak voltage in North America is
665   therefore $(120\text{V})(2)^{1/2}=170\text{V}$.

666   AC impedances $Z*(i\omega)$ are defined as $V*(i\omega)/I*(i\omega)$ and ac admittances $A*(i\omega)$ as
667    $I*(i\omega)/V*(i\omega)$. The imaginary components of $A*(i\omega)$ and $Z*(i\omega)$ are referred to as
668   reactances, and as shown below do not dissipate power.
669
670   *Resistances*
671   For a voltage $V=V_0\exp(-i\omega t)$ applied across a resistance R the current is
672

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

674
675   so that the impedance is
676

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

678
679   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
680   and independent of frequency.
681
682   *Capacitances*
683   For a capacitance C the current is
684

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

686
687   the capacitive impedance is
688

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

690
691   the capacitive admittance is
692

693    $$A_C^*(i\omega t)=-i\omega C.\qquad(2.87)$$

694
695   The capacitive admittance and admittance are therefore frequency dependent and imaginary.
696   Power dissipation per cycle in a capacitance is given by
697

$$P_C(t) = \langle V_C(t) I_C(t) \rangle = \langle \left[V_0 \exp(-i\omega t) \right] V_0 \left[-i\omega C_p \exp(-i\omega t) \right] \rangle = -V_0^2 \omega C_p \langle \exp(-2i\omega t) \rangle$$

698
$$= \langle -V_0^2 \omega C_p \left[\cos(-2\omega t) - i\sin(-2\omega t) \right] \rangle \tag{2.88}$$

$$= \langle -V_0^2 \omega C_p \left[\cos(2\omega t) + i\sin(2\omega t) \right] \rangle$$

$$= 0$$

699
700   because the averages of both $\cos(2\omega t)$ and $\sin(2\omega t)$ over one cycle are zero. The capacitive
701   impedance is therefore not a resistance if "resistance" is taken to imply power dissipation. This is
702   why an inductive or capacitive impedance is not considered to be an "ac resistance".
703
704   *Inductances*
705   For a self-inductance L the current is
706
707    $$I_L(\omega t) = \int \left(\frac{V}{L} \right) dt = \int \left(\frac{V_0 \exp(-i\omega t)}{L} \right) dt = \left(\frac{V_0}{L} \right) \frac{\exp(-i\omega t)}{-i\omega} \tag{2.89}$$

708
709   so that inductive impedance is
710
711    $$Z_L^*(i\omega t) = \frac{V^*(i\omega t)}{I_L^*(i\omega t)} = -i\omega L \tag{2.90}$$

712
713   and the inductive admittance is
714
715    $$A_L^*(i\omega t) = \frac{1}{-i\omega L} = \frac{i}{\omega L}. \tag{2.91}$$

716
717   The inductive reactance is therefore also imaginary and frequency dependent. Power dissipation
718   in an inductance is given by
719
720    $$P_L(t) = \langle V_L(t) I_L(t) \rangle = \langle \left[V_0 \exp(-i\omega t) \right] \left(\frac{V_0}{L} \right) \frac{\exp(-i\omega t)}{-i\omega} \rangle$$

$$= -\frac{V_0^2}{-i\omega L} \langle \exp(-2i\omega t) \rangle = \frac{V_0^2}{i\omega L} \langle \exp(-2i\omega t) \rangle = 0. \tag{2.92}$$

721
722   Thus the power dissipated by an inductance with no resistance is zero, just like that of a
723   capacitance.
724

725 *Parallel Resistance and Capacitance*

726   Consider a voltage $V = V_0 \cos(\omega t)$ applied across a resistance R_p in parallel with a

727 capacitance C_p. The current I_R through the resistance is

728

729 $$I_R = \frac{V}{R_p} = \frac{V_0 \cos(\omega t)}{R_p} = V_0 \cos(\omega t) G_p = \mathrm{Re}\left[V_0 G_p \exp(-i\omega t)\right]$$ (2.93)

730

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

732

733 $$\begin{aligned} I_C &= \frac{dq_C}{dt} = C_p \frac{dV}{dt} = -V_0 \omega C_p \sin(\omega t) \\ &= -V_0 \omega C_p \cos(\omega t - \pi/2) \mathrm{Re}\left[-iV_0 \omega C_p \exp(-i\omega t)\right] \end{aligned}$$ (2.94)

734

735 where q_C is the charge on the capacitor. Equation (2.94) implies that the sinusoidal (displacement)

736 current I_C lags the applied voltage by $\pi/2$ radians because $\sin(\omega t) = \cos(\omega t - \pi/2)$. The total

737 current through the parallel $R_p C_p$ circuit is

738

739 $$\begin{aligned} I = I_R + I_C &= V_0 G_p \cos(\omega t) - V_0 \omega C_p \sin(\omega t) \\ &= \mathrm{Re}\left[V_0 G_p \exp(-i\omega t)\right] + \mathrm{Re}\left[-iV_0 \omega C_p \exp(-i\omega t)\right] \\ &= \mathrm{Re}\left\{V_0\left[G_p - i\omega C_p\right]\exp(-i\omega t)\right\}. \end{aligned}$$ (2.95)

740

741 The phase relations for the current are therefore conveniently expressed by defining the parallel

742 combination of resistance and capacitance as a complex admittance A*

743

744 $$A^* = G_p - i\omega C_p,$$ (2.96)

745

746 or as a complex impedance Z*

747

748 $$Z^* = 1/A^* = \frac{1}{G_p - i\omega C_p} = \frac{G_p}{G_p^2 + \omega^2 C_p^2} + \frac{i\omega C_p}{G_p^2 + \omega^2 C_p^2}.$$ (2.97)

749

750 The complex capacitance is

751

752 $$C^* = \frac{A^*}{-i\omega} = C_p + \frac{iG_p}{\omega}$$ (2.98)

753

754 and the complex electric modulus is

755

756 $$M^*(i\omega) = 1/C^*(i\omega) = i\omega Z^*(i\omega).$$ (2.99)

757
758   Equation (2.97) is equivalent to
759

760 $$Z* = \frac{R_p}{1 + \omega^2 \tau_D^2} + \frac{iR_p \omega \tau_D}{1 + \omega^2 \tau_D^2}$$ (2.100)

761
762 where
763

764 $$\tau_D = R_p C_p$$ (2.101)

765
766 is the Maxwell relaxation time (the reason for the subscript D is given below).

767   When normalized by the cell constant k (dimensions m^{-1}) the quantities A^*, Z^* and C^* and
768 M^* become respectively the complex conductivity $\sigma^* = kA^*$, complex resistivity $\rho^* = Z^*/k$,
769 complex relative permittivity $\varepsilon^* = kC^*/e_0 = C^*/C_0$ (where C_0 is the capacitance of the
770 measuring cell in a vacuum, usually equated to that in air), and complex modulus M^*. Historically
771 the same symbol has been used for the complex electric modulus defined in terms of measured
772 circuit elements and as a material property, but this has not caused much (any?) confusion
773 probably because the inverse capacitance V/q has never been considered as a physically useful
774 quantity (in this respect it is not clear to this author why conductivity and resistivity should have
775 separate physical identities either).

776
777 *Series Resistance and Capacitance*
778   For a resistance R_s in series with a capacitance C_s
779

780 $$Z^*(i\omega) = R_s + \frac{1}{i\omega C_s} = R_s - \frac{i}{\omega C_s} = R_s \left(\frac{\omega \tau_E - i}{\omega \tau_E} \right),$$ (2.102)

781

782 $$A^*(i\omega) = \frac{R_s}{1 + \omega^2 R_s^2 C_s^2} + \frac{i\omega R_s^2 C_s}{1 + \omega^2 R_s^2 C_s^2} = \frac{R_s}{1 + \omega^2 \tau_E^2} + \frac{i\omega R_s \tau_E}{1 + \omega^2 \tau_E^2},$$ (2.103)

783

784 $$C^*(i\omega) = \frac{A^*(i\omega)}{-i\omega} = C_s \left(\frac{1 - i\omega R_s C_s}{1 + \omega^2 R_s^2 C_s^2} \right) = C_s \left(\frac{1}{1 + \omega^2 \tau_E^2} - \frac{i\omega \tau_E}{1 + \omega^2 \tau_E^2} \right),$$ (2.104)

785

786 $$M^*(i\omega) = i\omega Z^*(i\omega) = i\omega \left(R_s - \frac{i}{\omega C_s} \right) = i\omega R_s \left(\frac{\omega \tau_E - i}{\omega \tau_E} \right) = \frac{R_s}{\tau_E} (1 + i\omega \tau_E)$$ (2.105)

787
788 where $\tau_E = R_s C_s$ that is generally not equal to $\tau_D = R_p C_p$.
789   The relations between the four response functions are conveniently summarized by [1,10]
790

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

791
$$\Updownarrow \qquad\qquad\qquad \Updownarrow \qquad\qquad . \qquad\qquad (2.106)$$

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

792

793　　2.2.8.3 Experimental Factors

794　　*Cable Effects*

795　　　　Cable impedances can be analyzed using transmission line methods that invoke an infinite

796　　number of {L, C} components. One line of the cable is considered to be a series of inductances L

797　　and the other line as a zero impedance wire, with capacitances C connecting the two between

798　　every pair of inductances. In the limit of an infinite number of inductance and capacitance

799　　elements the cable impedance $Z_{cable} = (L/C)^{1/2}$ is real and constant. Coaxial cables are made so

800　　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

801　　short cable with a 50 Ω resistor across it looks like an infinitely long cable and a 50 Ω load on the

802　　cable has an ideal impedance match for maximum power transfer. Such a cable will also behave

803　　as an inductor if short circuited so that for a high conductivity attached sample resonance effects

804　　may be significant.

805

806　　*Electrode Polarization*

807　　　　This occurs for two and three terminal measurements when charge transfer does not occur

808　　between an electrode and the sample material, i.e. when the applied voltage is less than the

809　　decomposition potential of the sample (four terminal measurements are immune to this but they

810　　do not produce reliable capacitance data and require separate sample preparation). In this case the

811　　electrode-sample contact can be approximated as a capacitance C_s in series with the sample [11-

812　　13] that is much larger than the sample capacitance C_p. If the amplitude of the applied potential is

813　　too large (above the decomposition potential of the electrolyte) a Faradaic impedance [14, 15]

814　　will also occur in parallel with this capacitance [16] that can sometimes be approximated as a

815　　Warburg impedance (see §2.4.3).

816　　　　A series capacitance does not affect $M''(\omega)$ and simply adds $1/C_s$ to $M'(\omega)$: the total

817　　impedance $Z_{total}^*(i\omega)$ of the sample impedance $Z*(i\omega)$ and C_s is $Z_{total}^*(i\omega) = Z*(i\omega) + 1/i\omega C_s$

818　　so that

819

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

821

822　　It is a considerable advantage of the electric modulus function that $M''(\omega)$ is unaffected by

823　　electrode polarization and other high capacitance phenomena. This is exploited in some of the

824　　methods of data analysis discussed below but it should be noted that some researchers have

825　　correctly noted that M* also suppresses low frequency information (relative to ε* for example),

826　　but it can equally be claimed that ε* suppresses high frequency information. The low frequency

827　　high capacitance advantage of M* is not shared by the imaginary component of the resistivity ρ''

828　　because

829

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

831

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

833   Electrode polarization can however make the direct determination of the low frequency
834 quantities ε_0 and σ_0 difficult and sometimes impossible because it increases ε' above ε_0 at low
835 frequencies and, usually at lower frequencies, decreases σ' to below σ_0. Overlap between bulk
836 relaxations and these two electrode polarization effects prevents the observation of limiting low
837 frequency plateaus in $\varepsilon'(\omega)$ and/or $\sigma'(\omega)$. Although relaxation of electrode polarization often
838 occurs at much lower frequencies than the bulk relaxation,
839

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

841

842 the magnitude of the polarization dispersion can be very large [proportional to $(C_s - C_p) \approx C_s$]
843 and its high frequency tail can extend well into the bulk relaxation region. This phenomenon is
844 illustrated by the following representative average circuit quantities: a parallel capacitance
845 $C_p = 10 \, \text{pF}$ and parallel resistance $R_p = 10^7 \, \text{ohm}$ in series with a polarization capacitance of
846 $C_s = 10^4 \, \text{pF}$. Because both R_p and C_p will have distributions in a typical electrolyte there will be
847 dispersions in both ε' and σ' (see §2.4). The dispersion is centered around
848 $\omega \approx 1/(R_p C_p) = 10^4 \, \text{s}^{-1}$ and the low frequency plateau in ε' would normally then normally be
849 seen at ca. $\omega \approx 10^2 \, \text{s}^{-1}$, but this is dwarfed by the polarization capacitance at that frequency,
850 $C'_{pol}\left(\omega >> (R_p C_s)^{-1}\right) = C_s / \left(\omega^2 R_p^2 C_s^2\right) = 100 \, \text{pF}$, an order of magnitude higher than C_p. On the
851 other hand, the low frequency dispersion in conductivity due to polarization has barely begun at
852 $\omega = 10^2$: $\sigma_{ele} / \sigma_0 = \omega^2 \tau_{ele}^2 / \left(1 + \omega^2 \tau_{ele}^2\right) = 0.99$ for $\omega \tau_{ele} = \omega R_p C_s = \left(10^2\right)\left(10^{-1}\right) = 10$, where
853 the fact that the limiting high frequency conductivity for the Debye-like relaxation of electrode
854 polarization is σ_0:

855

$$\lim_{\omega \tau_{ele} \to \infty} \sigma'_{ele} = \frac{(\varepsilon_0 - \varepsilon_\infty)_{ele} \, e_0}{\tau_E} = \frac{(\varepsilon_0 - \varepsilon_\infty)_{ele} \, e_0 \varepsilon_\infty}{\tau_D \varepsilon_0} = \frac{(\varepsilon_0 - \varepsilon_\infty)_{ele} \, \sigma_0}{\varepsilon_0} \approx \sigma_0 \text{ for } \varepsilon_{0,ele} \gg \varepsilon_{\infty,ele} \tag{2.110}$$

857

858 Effects similar to electrode polarization can arise from other causes, such as poor electrode
859 contact where a capacitance due to air gaps occurs in parallel with a resistance at the contact
860 areas. Poor contacts have been shown to give spurious dielectric losses in undoped alkali halides
861 [17], and is suspected to be responsible for the poor reproducibility of other dielectric data for
862 alkali halides [18]. Space charge effects can also produce a series capacitance at the electrode

863   [19,20].
864
865   2.3   Dielectric Relaxation
866   An excellent resource for dielectric relaxation is ref. [3], particularly Chapter One by N. E.
867   Hill. An excellent review of dielectric relaxation phenomena in supercooled and glassy materials
868   is given by Richert [21] that also includes references to modern measurement techniques.
869
870   2.3.1   Frequency Domain
871   2.3.1.1 Dipole Rotation
872   A freely rotating dipole in a sinusoidally varying electric field with an angular frequency
873   ω low enough that the dipole can keep up with the field behaves as a pure capacitance C_{pure}. The
874   current then lags the field by π/2 radians and the complex admittance is
875
876    $$A^* = i\omega C_{pure}.$$ (2.111)
877
878   If the dipole cannot keep up with the field because of friction with its environment it will lag by
879   an additional angle δ and a component of the current appears in phase with the voltage and is
880   measured as a resistance. Equation (2.94) is then replaced by
881

882
$$
\begin{aligned}
I_C &= -V_0\omega C_p \cos(\omega t - \pi/2 - \delta) \\
&= -V_0\omega C_p \left[\cos(\omega t - \pi/2)\cos\delta + \sin(\omega t - \pi/2)\sin\delta \right] \\
&= -V_0\omega C_p \left[\sin(\omega t)\cos\delta - \cos(\omega t)\sin\delta \right],
\end{aligned}
$$ (2.112)

883
884   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
885    $V = +V_0 \cos(\omega t)$. This in phase component is of course zero when $\delta = 0$. Comparing eq. (2.112)
886   with eqs. (2.95) and (2.96) reveals that
887
888    $$A^* = \omega C_{pure} \sin\delta + i\omega C_{pure} \cos\delta$$ (2.113)
889
890   and
891
892    $$C^* = C' - iC'' = C_{pure} \cos\delta - iC_{pure} \sin\delta$$ (2.114)
893
894   so that
895
896    $$G_p(\text{effective}) = \omega C_{pure} \sin\delta$$ (2.115)
897
898   and
899
900    $$C_p(\text{effective}) = C_{pure} \cos\delta.$$ (2.116)

901
902 At low frequencies when the lag angle δ tends to zero the effective capacitance equals C_{pure} and
903 $G_p = 0$, as must be. When normalized by the geometric capacitance associated with the cell
904 constant k, $C_0 = e_0 / k$ where e_0 is the vacuum permittivity 8.854×10^{-12} F m^{-1}, the complex
905 capacitance becomes the complex permittivity, $\varepsilon^* = C^* / C_0$ so that

906
907 $$\varepsilon^* = \varepsilon' - i\varepsilon''$$ (2.117)

908
909 where

910
911 $$\varepsilon' = \frac{C_p}{C_0}(\varepsilon_0 - \varepsilon_\infty)\cos(\delta) + \varepsilon_\infty,$$ (2.118)

912 $$\varepsilon'' = \frac{G_p}{\omega \cdot C_0} = \frac{\sigma}{e_0 \cdot \omega} = \frac{C_p}{C_0}(\varepsilon_0 - \varepsilon_\infty)\sin(\delta),$$ (2.119)

913
914 and

915
916 $$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{G_p}{\omega C_p}.$$ (2.120)

917
918 Note that $\tan\delta$ is independent of the geometric capacitance C_0 and has the same frequency
919 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)
920 and (2.114) imply

921
922 $$A^* = i\omega C_0 \varepsilon^*$$ (2.121)

923
924 so that

925
926 $$\sigma^* = kA^* = i\omega e_0 \varepsilon^*$$ (2.122)

927
928 and

929
930 $$\rho^* = \frac{1}{\sigma^*} = \frac{1}{i\omega e_0 \varepsilon^*}$$ (2.123)

931
932   The complex electric modulus M* is defined as the reciprocal of ε^*:

933
934 $$M^* = 1 / \varepsilon^*$$ (2.124)

935
936 so that

937
938 $$M^* = i\omega C_0 Z^* = i\omega e_0 \rho^*.$$ (2.125)
939

940 The functions σ^*, ε^*, ρ^* and M^* are all analytical and their components all conform to the
941 Cauchy-Riemann and Kronig-Kramers equations. The relationships between them are given in
942 eq. (2.106).

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

945

946 $$\varepsilon^*(i\omega) = \varepsilon_\infty^E + \frac{\left(\varepsilon_0^E - \varepsilon_\infty^E\right)}{1 + i\omega\tau_E},$$ (2.126)

947 $$\varepsilon'(\omega) = \varepsilon_\infty^E + \frac{\left(\varepsilon_0^E - \varepsilon_\infty^E\right)}{1 + \omega^2\tau_E^2},$$ (2.127)

948
949 and
950

951 $$\varepsilon''(\omega) = \frac{\left(\varepsilon_0^E - \varepsilon_\infty^E\right)\omega\tau_E}{1 + \omega^2\tau_E^2},$$ (2.128)

952

953 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
954 constant electric field, respectively. Equations (2.127) and (2.128) yield a complex plane plot of
955 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
956 eliminating $\omega\tau_E$ between equations (2.127) and (2.128) (see Appendix C in Chapter One for
957 details).

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

959 $$\sigma'(\omega) = e_0\omega\varepsilon''(\omega) = \frac{e_0\left(\varepsilon_0^E - \varepsilon_\infty^E\right)\omega^2\tau_E}{1 + \omega^2\tau_E^2}$$ (2.129)

960
961 and
962

963 $$\sigma''(\omega) = e_0\omega\varepsilon_\infty^E + \frac{e_0\omega\left(\varepsilon_0^E - \varepsilon_\infty^E\right)}{1 + \omega^2\tau_E^2}.$$ (2.130)

964
965 Thus the real part of the conductivity of a Debye dielectric increases from zero at low frequencies
966 to a high frequency limit of
967

968 $\quad \sigma_\infty = \lim_{\omega \to \infty} \sigma'(\omega) = \mathrm{e}_0 \left(\varepsilon_0^E - \varepsilon_\infty^E \right) / \tau_E ,$ (2.131)

969

970 and the imaginary part diverges at high frequencies. Derivations of the Debye expressions for

971 $M'(\omega)$ and $M''(\omega)$ are instructive and straightforward but tedious – they are given in Appendix

972 2.1. The results are

973

974 $\quad M'(\omega) = M_0^E + \dfrac{\left(M_\infty^E - M_0^E \right) \omega^2 \tau_E^2}{1 + \omega^2 \tau_E^2}$ (2.132)

975

976 and

977

978 $\quad M''(\omega) = \dfrac{\left(M_\infty^E - M_0^E \right) \omega \tau_E}{1 + \omega^2 \tau_E^2} ,$ (2.133)

979

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

981 $\qquad$ If a limiting low frequency conductivity σ_0 is present that is not physically related to the

982 dielectric loss process (e.g. ionic conductivity in a dilute aqueous solution), it must be subtracted

983 from the measured conductivity before the dielectric loss is calculated from eq. (2.128).

984 Otherwise the limiting low frequency dielectric loss $\lim_{\omega \to 0} \varepsilon'' \to 0$ will be masked by the rapid rise

985 from the conductivity contribution

986

987 $\quad \lim_{\omega \to 0} \varepsilon'' = \lim_{\omega \to 0} \dfrac{\sigma_0}{\mathrm{e}_0 \omega} \to \infty .$ (2.134)

988

989 It has been argued that this subtraction is physically meaningful only if the conductivity is

990 unrelated to the dielectric loss process (as in the aqueous solutions just mentioned). If the

991 dielectric loss peak correlates with σ_0 as occurs in alkali silicate glasses [22-28] and other

992 ionically conducting liquids and glasses then the subtraction of σ_0 can be regarded as artificial

993 and other methods of data analysis are preferred (although this position is not universally held).

994 This is the principle reason for not using the complex permittivity in analyzing highly conducting

995 materials and is the subject of §2.4.

996 $\qquad$ If the decay function is nonexponential then dielectric relaxation can be described in terms

997 of a distribution of retardation times $g\left(\ln \tau_E \right)$ defined by the relations

998

999 $\quad \phi_E(t) = \int\limits_{-\infty}^{+\infty} g\left(\ln \tau_E \right) \exp\left(-\dfrac{t}{\tau_E} \right) d \ln \tau_E$ (2.135)

1000

1001 and

1002

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

1004
1005 so that eq. (2.126) generalizes to
1006

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

1008
1009 The generalization of eqs. (2.127) and (2.128) are
1010

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

1012
1013 and
1014

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

1016
1017 The nth moments of a distribution function are
1018

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

1020

1021 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

1022 example, $g\left(\ln\tau_E\right)$ is not renormalizable and a constant phase angle impedance can therefore be

1023 valid only over a limited range in relaxation times. In terms of $\phi(t)$ the moments are
1024

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

1026
1027 and
1028

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

1030

1031 2.3.1.2 Ionic Hopping
1032   Chapter One of [3] by N. E. Hill discusses the studies of Frohlich [6] and others on the
1033 dielectric relaxation consequences of two state models. We select here the Frohlich account of an
1034 entity that has only two possible equilibrium positions 1 and 2. The entity could be a molecular
1035 dipole or an ion for example. If the transition probabilities between the two positions are w_{12} and
1036 w_{21} when there is no applied field then a Debye relaxation with a single relaxation time
1037 $\tau_E = 1/(w_{12} + w_{21})$ is predicted that has an Arrhenius temperature dependence
1038 $\tau_E = A_E \exp(\Delta H / RT)$ where the pre-exponential factor A_E is a weak function of temperature and
1039 ΔH is the energy barrier that separates the two positions. As noted by Hill, however, a
1040 nonexponential decay function may result from local field effects.
1041
1042 2.3.2 Resonance Absorption
1043   The resonance expression for $\varepsilon^*(i\omega)$ is given by eq. 1.395 in Chapter One, repeated here
1044 for convenience:
1045

1046
$$\varepsilon^*(i\omega) = \frac{\omega_0^2 - \omega^2 + i\omega\gamma}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2\gamma^2} . \tag{2.143}$$

1047
1048 The corresponding expression for the real component of the conductivity is
1049

1050
$$\sigma'(\omega) = e_0\omega\varepsilon''(\omega) = \frac{e_0\omega^2\gamma}{\left(\omega_0^2 - \omega^2\right)^2 + \omega^2\gamma^2} . \tag{2.144}$$

1051
1052 For $\omega \ll \omega_0$, appropriate for almost all relaxation processes, eq. (2.144) becomes
1053

1054
$$\lim_{\omega \ll \omega_0} \sigma'(\omega) = \frac{e_0\omega^2\gamma}{\omega_0^4} , \tag{2.145}$$

1055
1056 so that $\sigma'(\omega)$ is proportional to ω^2. Since the strongest frequency dependence of conductivity
1057 for relaxation processes is ω power law exponents greater than unity imply a resonance process
1058 at high frequencies.
1059
1060 2.3.3 Time Domain
1061   Consider the case where an electric field E is "instantaneously" increased from zero to E_0
1062 across a dielectric sample at time $t = t'$ and kept constant thereafter, i.e. $E(t) = E_0 h(t - t')$ where
1063 $h(t)$ is the Heaviside function (eq. (1.327)). The initially randomized dipoles will partially orient
1064 themselves over time and the polarization and displacement will both increase (the final average
1065 orientation will not be complete because of thermal fluctuations):
1066
1067
$$D(t) = D(0) + \left[D(\infty) - D(0)\right]\left[1 - \phi_E(t)\right], \tag{2.146}$$

1068

1069   where $D(0)$ and $D(\infty)$ are the limiting short time (high frequency) and long time (low

1070   frequency) values of D(t) and $\phi_E(t)$ is the decay function for polarization at constant E

1071   corresponding to $D(t)$. The increase of D from zero to $D(\infty)$ is "instantaneous" compared with

1072   dielectric relaxation times (generally no shorter than about 10^{-11} s) and is due to polarization of

1073   molecular electron clouds that occurs roughly on optical time scales.

1074   It is sometimes convenient to approximate the relation between time domain data and

1075 $\varepsilon''(\omega)$ by the Hamon approximation

1076

1077 $$\varepsilon''(\omega) \approx \left(\varepsilon_0^E - \varepsilon_\infty^E\right)\left(\frac{-d\phi_E}{dt}\right)\left(\frac{5t}{\pi}\right),$$ (2.147)

1078

1079   obtained from the simplification that the normalized displacement current is given by

1080

1081 $$\left(\frac{-d\phi_E}{dt}\right) \sim t^{-n}.$$ (2.148)

1082

1083   No comparably simple relation exists between $\varepsilon'(\omega)$ and $\phi(t)$. Williams, Watt, Dev and North

1084   [29] have shown that for the Williams-Watt [30] decay function

1085

1086 $$\phi(t) = \exp\left[-\left(\frac{t}{\tau_0}\right)^\beta\right]$$ (2.149)

1087

1088   the Hamon approximation is accurate within 1% for $\omega\tau_0 > 1$ but fails for $\omega\tau_0 \leq 1$ and $\beta > 0.2$.

1089   Equation (2.147) therefore offers a high frequency approximation to the broadest frequency

1090   domain Williams-Watt functions that cannot be expressed in terms of named functions.

1091   The complex relative permittivity $\varepsilon^*(\omega)$ is related to the derivative of $\varepsilon(t)$ by

1092

1093 $$\varepsilon^*(i\omega) - \varepsilon_\infty^E = \left(\varepsilon_0^E - \varepsilon_\infty^E\right)\int_0^\infty -\left(\frac{d\phi_E}{dt}\right)\exp(-i\omega t)\,dt$$ (2.150)

1094

1095   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,

1096

1097 $$\phi_E(t) = \exp\left[-\left(\frac{t}{\tau_E}\right)\right],$$ (2.151)

1098

1099 and insertion of eq. (2.151) into eq. (2.150) yields the Debye equations (2.127) and (2.128)
1100 [Chapter One of ref. 3].
1101
1102 ### 2.3.4 Temperature Domain
1103 In many situations ω and τ_E are approximately interchangeable variables. Since τ_E often
1104 varies strongly with temperature a narrow temperature range can be used as a surrogate for a wide
1105 frequency range. The temperature dependence of τ_E is often approximated by the Arrhenius
1106 relation
1107

1108
$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right),\tag{2.152}$$

1109
1110 where τ_0 is independent of temperature, R is the ideal gas constant, and E_a is the activation
1111 energy. A better approximation is the Fulcher equation
1112

1113
$$\tau_E = A_F \exp\left(\frac{B_F}{T - T_0}\right)\tag{2.153}$$

1114
1115 where A_F, B_F and T_0 are positive constants. Thus the variables $\ln(\omega\tau)$ at constant ω, and E_a/RT
1116 or $B_F/(T - T_0)$, are equivalent for a single relaxation time dielectric. In this case eqs. (2.152) and
1117 (2.153) indicate that over the convenient temperature range from liquid nitrogen (77 K) to room
1118 temperature (300K) the retardation time can vary over a very large range. For example τ changes
1119 by a factor of 10^{25} for an average activation energy of 50 kJ/mol. The temperature variable is
1120 therefore extremely useful for scans of the total relaxation spectrum and is frequently used for
1121 polymers whose relaxation behavior is typically characterized by widely separated and broad
1122 relaxation processes. Activation energies E_a are obtained from plots of log frequency $\ln f$ against
1123 the inverse temperature $1/T_{max}$ at which ε'' or $\tan\delta$ passes through its maximum:
1124

1125
$$\left\langle\frac{E_a}{R}\right\rangle = -\left[\frac{d\ln f}{d(1/T)}\right].\tag{2.154}$$

1126
1127 It has been reported [32] that the activation energy obtained in this way is ambiguous because it
1128 depends on whether the derivative is determined in the isothermal frequency domain or in the
1129 temperature domain at constant frequency: the frequency domain plot of $\ln f_{max}$ vs. $1/T$ was found
1130 to be strongly curved whereas the plot of $\ln f$ vs. $1/T_{max}$ was found to be linear.
1131 Although temperature is useful because of its experimental convenience it is not
1132 quantitative because "everything changes with temperature". For example the dispersion
1133 $\left(\varepsilon_0^E - \varepsilon_\infty^E\right)$ can only be estimated because ε_0^E and to a less extent ε_∞^E are temperature dependent,
1134 although it can be estimated from the relation [33]
1135

1136 $$\left(\varepsilon_0^E - \varepsilon_\infty^E\right) \approx \left(\frac{2}{\pi R}\right)\left\langle\frac{1}{E_A}\right\rangle^{-1} \int_0^\infty \varepsilon''(T)\, d\left(1/T\right).$$ (2.155)

1137

1138 Equation (2.155) is an approximation because of two assumptions in its derivation that must be

1139 made for mathematical tractability: (i) $\left(\varepsilon_0^E - \varepsilon_\infty^E\right)$ is independent of temperature [32] and (ii)

1140 $\langle E_a\rangle = \langle 1/E_a\rangle^{-1}$ (not generally true because of the Schwarz inequality eq. 1.333):.

1141

1142 $$\langle E_A\rangle\langle 1/E_A\rangle^{-1} \geq 1.$$ (2.156)

1143

1144 There are two situations where $\ln\omega$ and E_a/RT are not even approximately equivalent:

1145 (i) functions for which ω and τ_E are not invariably multiplied together (for example the

1146 conductivity of a Debye dielectric, eq. (2.128));

1147 (ii) distributions of retardation times that change with temperature.

1148

1149 2.3.5 Equivalent Circuits

1150 The electrical response for an exponential dielectric decay function, the Debye relations

1151 eqs. (2.127) and (2.128) plus any separate conductivity contribution σ_0, is simulated by an

1152 equivalent circuit comprising three parallel arms: a capacitance C_p, a series combination of R_s

1153 and C_s, and a resistance R_p. The relaxation part of the circuit is the series component $R_s + C_s$,

1154 the parallel resistance R_p corresponds to the separate conductivity, and the parallel capacitance

1155 C_p simulates the limiting high frequency permittivity. If for a particular range of frequencies the

1156 equivalent circuit of an experimental sample resembles $R_s + C_s$ and the frequency range

1157 encompasses $\omega = 1/\left(R_s C_s\right)$ then a dielectric loss peak will be observed in that frequency range. An

1158 example is electrode polarization in a conducting medium that at low frequencies is approximated

1159 by an electrode capacitance in series with the low frequency resistance of the sample. In this case

1160 a dielectric loss is observed with a retardation time given by the product of the polarization

1161 capacitance and sample resistance. Electrode polarization effects in solid electrolytes can often be

1162 a serious problem; they were briefly discussed in §2.2.8.3 and are discussed in detail in §2.3.6.1

1163 and §2.3.6.4 below.

1164 In terms of the equivalent circuit the components of the complex permittivity are (see

1165 Appendix 2.3)

1166

1167 $$\varepsilon'(\omega) = \frac{\sigma''}{e_0\omega} = \left(\frac{1}{C_0}\right)\left(C_p + \frac{C_s}{1 + \omega^2\tau_E^2}\right)$$ (2.157)

1168

1169 and

1170

1171 $$\varepsilon''(\omega) = \frac{\sigma'}{e_0\omega} = \left(\frac{C_s}{C_0}\right)\left(\frac{\omega\tau_E}{1+\omega^2\tau_E^2}\right) + \frac{\sigma_0}{e_0\omega},$$ (2.158)

1172
1173 that reproduce the Debye relations eqs. (2.127) and (2.128). The low and high frequency limits of
1174 ε' are
1175

1176 $$\lim_{\omega\to 0}\varepsilon'(\omega) = \varepsilon_0 = \left(\frac{C_p + C_s}{C_0}\right)$$ (2.159)

1177
1178 and
1179

1180 $$\lim_{\omega\to\infty}\varepsilon'(\omega) = \varepsilon_\infty = \left(\frac{C_p}{C_0}\right).$$ (2.160)

1181

1182 Matlab®/GNUOctave codes for computing $M^*(i\omega)$ and $\rho^*(i\omega)$ with the added R$_p$ are given in

1183 Appendix 2.2. A notable result is that $M^*(i\omega)$ exhibits two relaxations corresponding to the

1184 Debye relaxation and an additional relaxation due to σ_0. The Debye relaxation for $M^*(i\omega)$ is

1185 unaffected by R$_p$ but the conductivity relaxation due to σ_0 is.

1186   As noted in §2.1 the occurrence of a dielectric and conductivity relaxation together raises
1187 an important nomenclature issue that has produced much confusion: the subscripts for denoting
1188 limiting low and high frequency limits can be ambiguous because these limits can refer to either
1189 the average dielectric relaxation frequency or to the average conductivity relaxation frequency. In
1190 particular, the quantity ε_∞ that enters into the expression for the conductivity relaxation time,
1191 $\langle\tau_D\rangle = e_0\varepsilon_\infty/\sigma_0$, is the high frequency limit for the conductivity relaxation, that may correspond
1192 to the low frequency limit for a separate dielectric relaxation. A proposed nomenclature to resolve
1193 this ambiguity was given above in §2.1 and has already been used in this section.
1194

1195 2.3.6 Interfacial Polarization
1196   In a homogeneous material $\vec{\nabla}\cdot\vec{D} = e_0\varepsilon\vec{\nabla}\cdot\vec{E} = 0$ implies $\vec{\nabla}\cdot\vec{E} = 0$. At the interface between
1197 two dielectric materials of different permittivity, however, there is a discontinuity in ε and
1198 $\vec{\nabla}\cdot\vec{D} = 0$ no longer implies $\vec{\nabla}\cdot\vec{E} = 0$. The solution to this problem is obtained by applying
1199 Gauss's and Stokes' theorems to the interface with the result that the component of $\vec{E}$ tangential
1200 to the interface is continuous across the interface and the normal component of $\vec{D}$ is either
1201 continuous (no interfacial charge) or discontinuous if there is a free charge that is not the result of
1202 polarization of the materials on each side of the interface. These boundary conditions make
1203 macroscopic interfacial effects dependent on the geometry of the interface.
1204   Relaxation of interfacial polarization between alternating slabs of insulating dielectric and
1205 conducting layers, generically referred to as a Maxwell Layered Dielectric, is characterized by a
1206 single relaxation time τ_i given by

1207

1208 $$\tau_i = R_s C_s = \left(\frac{\ell_R}{\ell_C}\right) e_0 \rho \varepsilon = \left(\frac{\ell_R}{\ell_C}\right)\left(\frac{e_0 \varepsilon}{\sigma}\right) \qquad (2.161)$$

1209

1210 where ℓ_R is the thickness of the resistive layer with material resistivity ρ and ℓ_C is the thickness
1211 of the capacitive layer with material permittivity ε.
1212

1213   2.3.7   Maxwell-Wagner Polarization
1214   Relaxation of interfacial polarization between a conducting sphere embedded in a
1215 dielectric continuum is known as Maxwell-Wagner (MW) polarization. Wagner [34] computed
1216 the loss tangent $(\tan \delta)$ for a volume fraction ϕ of spheres of material conductivity σ_1 and
1217 relative permittivity ε_1 suspended in a dielectric medium of relative permittivity ε_2, that was then
1218 generalized by Sillars [35] to suspensions of nonspherical particles. An excellent discussion of the
1219 phenomenon is given in ref [3] from which much of the following is distilled. We also draw from
1220 the paper by van Beek [36] who gave the Sillars formula and then considered the special case of
1221 suspended spheres, and noted that the often cited Wagner formula is only correct when the
1222 permittivities of the suspended material and the dielectric medium are equal and that the Sillars
1223 expression does not have this flaw.
1224   The Sillars expression for aspherical particles with aspect ratio a/b and a parallel to the
1225 field direction is
1226

1227 $$\tan \delta = \frac{\varepsilon_2 K}{\left[e_\infty\left(\varepsilon_2 K + e_\infty\right)\right]^{1/2}}\left(\frac{\omega \tau_0}{1 + \omega^2 \tau_0^2}\right), \qquad (2.162)$$

1228
1229 with
1230

1231
$$K = \frac{n^2 \phi \varepsilon_2}{\left[(n-1)\varepsilon_2 + \varepsilon_1\right]} \qquad (a),$$

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

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

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

$$(2.163)$$

1232
1233 where n is a function of the aspect ratio a/b. The limiting values for n are
1234

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

1235
$$n = 3 \qquad\qquad (a = b) \qquad (b) \qquad\qquad\qquad (2.164)$$

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

1236
1237 Equation (2.164)(c) indicates that for needle-like particles oriented in the direction of the field the
1238 value of n can be large – for example n ~ 50 for a = 10b. Because $\tan\delta$ is roughly proportional to
1239 n^2 [eqs. (2.162) and (2.163)a] the Maxwell-Wagner-Sillars effect can produce very large dielectric
1240 losses. For spherical particles
1241

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

1242
$$e_\infty = \varepsilon_2 \left[1 + \frac{3\phi(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_2 + \varepsilon_1} \right] \qquad (b), \qquad\qquad\qquad (2.165)$$

$$T = \frac{e_0 \left[2\varepsilon_2 + \varepsilon_1 \right]}{\sigma_1} \qquad (c),$$

1243
1244 and τ_0 is again given by eq. (2.163)d. The maximum value of $\tan\delta$ computed from eq. (2.162)d
1245 is therefore
1246

1247
$$\tan\delta_{\max} = \frac{\varepsilon_2 K}{2 \left[e_\infty (\varepsilon_2 K + e_\infty) \right]^{1/2}} \,. \qquad\qquad\qquad (2.166)$$

1248
1249 This expression is inconveniently complicated but simplifies when $\phi \to 0$:
1250

1251
$$\lim_{\phi \to 0} \left(\tan\delta_{\max} \right) = \frac{9\phi\varepsilon_2}{2(2\varepsilon_2 + \varepsilon_1)} \,. \qquad\qquad\qquad (2.167)$$

1252
1253 The components of the complex relative permittivity for the Maxwell-Wagner phenomenon for
1254 this limiting case are conveniently expressed using three ancillary functions [36]:
1255

1256
$$\varepsilon_\phi = \varepsilon_2 \left\{ 1 + \frac{3\phi(\varepsilon_1 - \varepsilon_2)}{2\varepsilon_2 + \varepsilon_1} \right\}, \qquad\qquad\qquad (2.168)$$

1257

1258
$$S = \frac{9\phi\varepsilon_2}{2\varepsilon_2 + \varepsilon_1} \,, \qquad\qquad\qquad (2.169)$$

1259

1260 $$T = \frac{\sigma_1}{e_0(2\varepsilon_2 + \varepsilon_1)} \, . \tag{2.170}$$

1261
1262 Then
1263

1264 $$\varepsilon'' = \frac{(\varepsilon_\phi S \omega T)}{1 + \omega^2 T^2} \tag{2.171}$$

1265
1266 and
1267

1268 $$\varepsilon' = \varepsilon_\phi \left\{ 1 + \frac{S}{1 + \omega^2 T^2} \right\} . \tag{2.172}$$

1269
1270 The maximum in the observed dielectric loss ε''_{MW} is therefore
1271

1272 $$\varepsilon''_{max} = \frac{9\phi\varepsilon_2^2}{2(2\varepsilon_2 + \varepsilon_1)} \left[1 + \frac{3\phi(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_{12} + \varepsilon_1} \right] \rightarrow \frac{9\phi\varepsilon_2^2}{2(2\varepsilon_2 + \varepsilon_1)} \, , \tag{2.173}$$

1273
1274 that occurs at an angular frequency ω_{max} given by
1275

1276 $$\omega_{max} = 1/\tau_{MW} = \frac{\sigma_1}{e_0(2\varepsilon_1 + \varepsilon_2)} \, . \tag{2.174}$$

1277
1278 At ω_{max} the value of ε' from eq. (2.172) is $\lim_{\phi \to 0} \varepsilon' = \varepsilon_2$ that when combined with eq. (2.173)

1279 produces eq. (2.167).

1280
1281 2.3.8 Examples
1282   Attention is restricted to the dielectric relaxation of water molecules in different
1283 environments.

1284
1285 2.3.8.1 Liquid Water
1286   Water is one of the few liquids that relaxes with a single retardation time (or very close to
1287 it) and therefore has a Debye complex permittivity. Its dielectric relaxation frequency depends on
1288 temperature but always lies within the microwave region of the em spectrum. This has important
1289 implications for both navigational and meteorological radar and is of course the basis for
1290 microwave cooking. The temperature dependence of the retardation time is not Arrhenius but
1291 rather adheres to the empirical Fulcher equation (1.543) and (2.153), repeated here for
1292 convenience:

1293

1294 $$\tau = A_F \exp\left(\frac{B_F}{T - T_0}\right), \qquad\qquad\qquad (2.175)$$

1295

1296 with parameters $A_F = 1.25 \times 10^{-13}$ s, $B_F = 669$ K, $T_0 = 138$ K that give a good description of $\tau(T)$

1297 down to the limit of supercooling of bulk water, ca. -35^0 C. The relaxation frequency $(1/2\pi\tau)$

1298 therefore varies between 62 GHz at 0° C and 74 GHz at 100 ^{o}C and the energy absorption at 100

1299 ^{o}C is about 75% that at 0 ^{o}C. Microwave ovens generally operate at a frequency 2.45 GHz that

1300 lies on the low frequency side of the Debye dielectric loss peak - the dielectric losses at this

1301 frequency are about 4.0% and 3.3% of the maximum loss. The fact that the frequency of a

1302 microwave oven is on the lower side of the dielectric loss peak of water means that energy

1303 absorption decreases with increasing temperature as the loss peak moves to higher frequencies,

1304 thus preventing runaway heating.

1305

1306 2.3.8.2 Supercooled Water

1307   Maxwell-Wagner polarization has been used to obtain the relative permittivity of

1308 supercooled water down to about -35^0C [37, 38]. The Maxwell-Wagner losses occur in the

1309 frequency range $10^5 - 10^6$ Hz that is far below the frequency range for the dielectric relaxation of

1310 water (around 10^{11} Hz) so that the measured values for the relative permittivity correspond to the

1311 limiting low frequency value $\varepsilon_0 >\sim 80$. This range is also far above the relaxation frequency for

1312 ice that is about $10^{3.5}$ Hz at 0^oC and decreases with decreasing temperature, so that if

1313 crystallization occurred the relevant relative permittivity of ice is the limiting high frequency

1314 value $\varepsilon_\infty \sim 5$, far smaller than the limiting low frequency value $\varepsilon_0 >\sim 80$ It is fortunate that the

1315 Maxwell-Wagner losses occur at frequencies between the relaxation frequency ranges of water

1316 and ice and do not overlap with either.

1317   Emulsions of water in heptane stabilized by the surfactant sorbitol tristearate [37] and

1318 droplets suspended in beeswax [38] both exhibit Maxwell-Wagner polarization. In the first and

1319 rigorous beeswax study by Hasted and Shahidi [38] volume fractions of 0.5% and 1.0% were

1320 used. Hodge and Angell [37] later used a much larger volume fraction of water (30%) that was

1321 necessitated by their much lower instrumental sensitivity. Their data were stated to be

1322 inconsistent with the Maxwell-Wagner formulae because the observed values of ε''_{max} were

1323 claimed to be about four times larger than predicted and their sign of $(d\varepsilon''_{max}/dT) \propto (d\varepsilon_1/dT)$ was

1324 positive rather than negative as predicted by their eq. (3). However their eq. (3) is incorrect – the

1325 numerator term ε_2^2 of eq. (2.173) was given as ε_1^2 so that the analyses of ε^*_{MW} given in [1] and

1326 [37] are both incorrect. Equation (2.173) predicts that ε''_{max} is indeed inversely proportional to ε_1

1327 if $\varepsilon_1 \gg \varepsilon_2$ (a good approximation for water droplets in hexane). The analyses in terms of the

1328 electric modulus [1,37] are unaffected by this mistake and remain valid although the stated

1329 requirement that a series capacitance that simulates the surfactant layer around the droplet needs

1330 to be large for the modulus analysis to be useful [1] is not correct (see eq. (2.107) above).

1331   The observed maxima in ε'' decreased with decreasing temperature that is consistent with

1332 eq. (2.173), but for $\varepsilon_1 \approx 100 \gg \varepsilon_2 \approx 2$ and $\phi = 0.3$ the predicted value is about

1333 $\varepsilon''_{max} \approx \{(9)(0.3)(4)/[2(106)]\} \approx 0.005$, compared with the experimental values that range

1334 between about $0.4 - 0.8$. The observed value is therefore too large by a factor of about 100. Also,

1335 the measured ratio of ε''_{max} at the temperature extremes of 0°C and -35°C is about 1.8 compared

1336 with the correct value of about 1.2. The observed values of ω_{max} for ε'' were centered

1337 around $2\pi(5.5 \times 10^6 Hz) \approx 3.5 \times 10^7$ rad/s from which eq. (2.174) predicts a conductivity of about

1338 $\sigma_1 \approx e_0\left[(2\varepsilon_1 + \varepsilon_2) + \phi(\varepsilon_1 - \varepsilon_2)\right]\omega_{max}/(1-\phi) \approx (9 \times 10^{-12}\,\text{F/m})(230)(3.5 \times 10^7)/0.7$

1339 $\approx (9 \times 10^{-12}\,\text{F/m})(230)(3.5 \times 10^7)/0.7 \approx 0.1\,\text{S/m}$, that is impossibly high.

1340 The measured modulus peak heights also decreased with decreasing temperature and since

1341 M''_{max} is assumed to be inversely proportional to the permittivity this trend is also in the correct

1342 direction. Values of ε_1 for water were then derived by assuming that $M''_{max} \propto 1/\varepsilon_1$, fixing the

1343 proportionality constant from literature data for ε_1 at $0\ ^{0}$C and then least squares fitting a

1344 quadratic in temperature to eight data points between 0^{0}C and $-35\ ^{0}$C. Agreement with the earlier

1345 results, of which the authors were unaware at the time of paper submission (see Note added in

1346 Proof in [37]), was within the $\pm 2\%$ uncertainties claimed for each method but the agreement is

1347 better than this because most of the discrepancies are systematic due to the different values of ε_1

1348 at 0°C for the two methods (measured in [38] but chosen from the literature as a proportionality

1349 constant in [37]). When this is corrected for by equating the average of the modulus derived

1350 permittivities to the average from reference [38] the differences are reduced to 0.5% or less. This

1351 is a remarkable result given the simplifications used in the modulus analysis.

1352 These Maxwell-Wagner results can be rationalized in terms of a simplified equivalent

1353 circuit for the emulsified water droplets: a parallel (R_1C_1) element (corresponding to the water

1354 droplet with relative permittivity ε_1 and conductivity σ_1) is in series with a capacitance C_s that

1355 simulates the suspected thin layer of emulsifier, and a capacitance C_2 in parallel with the series

1356 combination to simulate the surrounding heptane. Intuitively C_2 is much smaller than C_1 from

1357 both geometrical and physical considerations $(\varepsilon_2 \ll \varepsilon_1)$. The circuit analysis is:

1358 (i) Admittance A_1 of parallel (R_1C_1) element:

1359 $A_1 = 1/R_1 + i\omega C_1 = (1 + i\omega R_1 C_1)/R_1 = (1 + i\omega\tau_1)/R_1$ so that

1360

1361 $Z_1 = R_1/(1 + i\omega\tau_1).$ (2.176)

1362

1363 (ii) Impedance of $\{(R_1C_1) + C_s\}$ arm $= Z_{1s} = \dfrac{R_1}{1 + i\omega\tau_1} + \dfrac{1}{i\omega C_s} = \dfrac{i\omega R_1 C_s + 1 + i\omega\tau_1}{i\omega C_s(1 + i\omega\tau_1)} \Rightarrow$

1364

1365 $A_{1s} = \dfrac{i\omega C_s(1 + i\omega\tau_1)}{1 + i\omega(\tau_1 + R_1 C_s)}.$ (2.177)

1366

1367   (iii)   Admittance A_{1s2} of complete circuit:

1368 $A_{1s2} = A_{1s} + i\omega C_2 = \dfrac{i\omega C_s - \omega^2 C_s \tau_1 + i\omega C_2 \left[1 + i\omega\left(\tau_1 + R_1 C_s\right)\right]}{1 + i\omega\left(\tau_1 + R_1 C_s\right)} =$

1369

1370 $\dfrac{i\omega\left(C_s + C_2\right) - \omega^2\left(C_s\tau_1 + C_2\tau_1 - R_1 C_s C_2\right)}{1 + i\omega\left(\tau_1 + R_1 C_s\right)}.$ (2.178)

1371

1372   (iv)   For $C_2 \ll C_1$ appropriate for water droplets in heptane the total admittance simplifies to

1373

1374 $A_{1s2} = \dfrac{i\omega C_s - \omega^2 R_1 C_1 C_s}{1 + i\omega R_1\left(C_1 + C_s\right)}.$ (2.179)

1375
1376   Thus
1377

$$C_{1s2}^* = \dfrac{A_{1s2}}{i\omega} = \dfrac{C_s\left(1 + i\omega R_1 C_1\right)}{1 + i\omega R_1 C_s} = \dfrac{C_s\left(1 + i\omega R_1 C_1\right)\left(1 + i\omega R_1 C_s\right)}{1 + \omega^2 R_1^2 C_s^2}$$

1378 $$= \dfrac{C_s - \omega^2 R_1^2 C_1 C_s}{1 + \omega^2 R_1^2 C_s^2} + \dfrac{i\omega C_s R_1\left(C_1 + C_s\right)}{1 + \omega^2 R_1^2 C_s^2}.$$ (2.180)

1379
1380   so that
1381

1382 $C'' = \dfrac{\omega C_s R_1\left(C_1 + C_s\right)}{1 + \omega^2 R_1^2 C_s^2}.$ (2.181)

1383

1384   The maximum value $\left(C_1 + C_s\right)/2$ for C'' is therefore determined in part by the surfactant layer
1385   and is greater than the value $C_1/2$ for no series capacitance. This is consistent with the observed
1386   maxima in ε'' [37] being about 100 times greater than that calculated from the Maxwell-Wagner
1387   expression. The maximum in C'' also occurs at $\omega_{max} = 1/\left(R_1 C_s\right)$ that is also determined in part by
1388   the surfactant layer and therefore would give an incorrect value for the conductivity of water. This
1389   dependency of the relaxation time on C_s can also account for the (unreported) fact that changing
1390   the suspending medium changed ω_{max} [37] since the suspending medium would be expected to
1391   affect the surfactant layer and C_s.
1392   The imaginary component of the electric modulus for the same circuit when $C_2 \ll C_1$ is
1393

1394 $M'' = \dfrac{i\omega R_1}{\left(1 + i\omega^2 R_1^2 C_1^2\right)} = \left(\dfrac{1}{C_1}\right)\dfrac{i\omega R_1 C_1}{\left(1 + i\omega^2 R_1^2 C_1^2\right)},$ (2.182)

1395

1396   the maximum value of which is $1/(2C_1)$ and therefore contains the desired information about C_1

1397   that is independent of C_s. The frequency of maximum M" is $\omega_{max} = 1/(R_1 C_1)$ and is also

1398   independent of C_s.

1399   Matlab® and GNUOctave calculations of the relaxation functions for the circuit enable

1400   values of the circuit elements to be quickly estimated that produce trends that are generally

1401   consistent with the experimental data, with the notable exception of the maximum values of ε"

1402   (discussed briefly below). For example good agreement with the experimental trends is attained

1403   with $R_1 = 10^3\,\Omega$; $C_1 = 10^{-3}\,F$; $C_2 = 10^{-5}\,F$; $C_s = 5 \times 10^{-4}\,F$. The value of 100 for the ratio C_1/C_2

1404   was chosen to approximate the ratio of permittivities of water and hexane and to accommodate an

1405   unknown geometric factor for the suspending medium relative to the droplet, and the value of C_s

1406   was found from the experimental ratio of 0.5 for the frequencies of maximum $\varepsilon"$ and M" (the

1407   latter being higher). The geometric factor is probably the largest source of uncertainty in

1408   estimating the values of the circuit parameters.

1409   The Maxwell-Wagner equivalent circuit discussed here is obviously crude but serves to

1410   rationalize the remarkable success of the electric modulus in analyzing the Maxwell-Wagner

1411   effect for water droplets in a dielectric medium of low permittivity.

1412

1413   2.3.8.3 Hydration Water

1414   Water of ionic hydration is readily probed by temperature domain dielectric relaxation if

1415   the ionic conductivity contribution to $\varepsilon"$ and $\tan\delta$ is sufficiently small, such as sometimes

1416   occurs in hydrate glasses. Data for $Ca(NO_3)_2$ hydrate glasses [39] provide a convenient

1417   illustration of how water in different molecular environments can be distinguished dielectrically.

1418   Spectra of dielectric $\tan\delta$ vs. 1/T at 1 Hz were shown for eight glasses of composition

1419 $Ca(NO_3)_2 . RH_2O$ (R = 3, 4, 5, 6, 8, 10, 12, 14). Glasses with lower R values required the

1420   addition of KNO_3 to ensure glass formation but this was expected to have only a minor effect on

1421   water dynamics because water was expected to be much more strongly bound to Ca^{2+} because of

1422   its larger ionic charge/radius compared with K^+. Four relaxations were observed labeled as α, β, γ,

1423   δ:

1424 (α) A conductivity relaxation at low $1/T$ corresponding to the onset of conductivity at glass

1425   transition was manifested as a steep increase in $\tan\delta$. The relaxation temperature corresponds to

1426 $\tan\delta = 1$ and will be referred to here as the "conductivity wing". It is essential that this relaxation

1427   occur at sufficiently high T in order that the other relaxations occur in the poorly conducting

1428   glassy state and not be hidden beneath the conductivity contribution to $\tan\delta$.

1429 (β) A dielectric relaxation lying close to the conductivity wing whose shift in position with R

1430   paralleled that of the conductivity relaxation. It was observable only as a shoulder for $R = 1 - 6$

1431   and (probably) R = 10 but is seen as a distinct peak for $R \approx$ trace.

1432 (γ) A weak low temperature dielectric relaxation $(\tan\delta_{max} \approx 10^{-3} - 10^{-2})$ was observed as a

1433   broad maximum for R = 4, 5, 6 and as a shoulder for $R \geq 8$.

1434 (δ) A dielectric relaxation whose intensity increased rapidly with R. It was probably a part of

1435   the broad maximum near $10^3/T \approx 7.5$ for R = 8 but appeared as a clear maximum for $R \geq 10$.

1436   The β relaxation was assigned to cation bound water that for the reason given above
1437 probably coordinates Ca^+ rather than K^+. The rapid shift in relaxation temperature with R > 1 was
1438 interpreted as a change in water dynamics as H_2O replaces NO_3^- in the first coordination shell of
1439 Ca^+. The *R* invariance for *R* = trace and R = 1 was attributed to a single water molecule lying in
1440 the first coordination shell. This assignment of the β relaxation to Ca^{2+} bound water implied a
1441 dielectric activity that merits discussion. The most plausible geometry for H_2O coordinated to Ca^+
1442 is when the H_2O dipole points away from the Ca+ ion. However if this held in the complex ionic
1443 environment of the glass there would be no dielectric activity because the rotational axis would
1444 bisect the H-O-H angle and coincide with the dipole vector. Two alternatives suggest themselves:
1445 (1)   Exchange of water and nitrate in the coordination shell. This implies an associated volume
1446 fluctuation and ultrasonic activity. Such activity has been observed [40,41] in $Ca(NO_3)_2 \cdot RH_2O$
1447 solutions at about 20 MHz at room temperature. This relaxation moved to higher frequencies with
1448 increasing R and the edge of a second relaxation at higher frequencies was noted, both being
1449 consistent with the glassy state dielectric behavior. Such an exchange would also be expected to
1450 contribute to the translational ionic migration that produces conductivity, consistent with the
1451 essentially R − invariant difference between the α and β relaxation temperatures. The
1452 possibility that this relaxation is part of a conductivity relaxation with a distribution of relaxation
1453 times is discussed in §2.5.
1454 (2)   A different $Ca^+\text{-}OH_2$ geometry in which the dipole vector and rotation axis do not
1455 coincide. Neutron diffraction data indicate this occurs in $CaCl_2$ and $NiCl_2$ solutions [42], in
1456 which an angle of ca. 40° was observed between the dipole and coordination axes at R = 12.6
1457 $\left(NiCl_2\right)$ and 12.3 $\left(CaCl_2\right)$, and about 0° in dilute solutions $\left(R \approx 450\right)$. It was not possible to find
1458 the dielectric activity per water molecule of the β relaxation in the $Ca(NO_3)_2 \cdot RH_2O$ glasses
1459 because of overlap with the conductivity wing and the γ relaxation, but for the mixed nitrate
1460 glasses the well defined conductivity wing for the anhydrous mixture could be shifted and
1461 subtracted to yield plausibly shaped peaks of $\tan \delta$ vs. $1/T$. The peak heights and widths in the R
1462 = 1 and R = 3 glasses were about the same so that barring an unlikely ratio of activation energies
1463 in excess of 3 it appears that the dielectric activity per water molecule does indeed decrease with
1464 increasing R. A crude calculation yielded sensible values of $\Delta\theta$ from the observed values of
1465 $\tan \delta_{max}$: the dipole being relaxed was assumed to be the component of the water dipole $\left(\mu_W\right)$
1466 orthogonal to the rotation axis, magnitude $\mu_W \sin\left(\Delta\theta\right)$, and $\tan \delta_{max}$ was assumed to be
1467 proportional to $\left(\varepsilon_0 - \varepsilon_\infty\right)$ that is in turn proportional to $R\left[\mu_W \sin\left(\Delta\theta\right)\right]^2$. Equating $\tan \delta_{max}$ for
1468 the 1*R* and 3*R* glasses then yielded
1469
1470 $$\frac{3}{T_{3R}}\sin^2\left(\Delta\theta_{3R}\right) = \frac{1}{T_{1R}}\sin^2\left(\Delta\theta_{1R}\right),$$ (2.183)
1471
1472 so that
1473

1474 $$\sin^2\left(\Delta\theta_{3R}\right) \approx 0.286 \sin^2\left(\Delta\theta_{1R}\right).$$ (2.184)

1475

1476 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

1477 comparable with the neutron diffraction values.

1478   For large values of R the δ relaxation was expected to resemble that of pure water so that

1479 an extrapolation to infinite dilution could yield the temperature at which the relaxation frequency

1480 of water is 1 Hz. The relaxation temperatures at 1 Hz for the δ relaxation in four glasses

1481 (Ca(NO$_3$)$_2$, CaZnCl$_4$, Li$_2$ZnCl$_4$ and ZnCl$_2$ hydrates) all extrapolated to 162 ± 5 K at infinite

1482 dilution, suggesting that the relaxation temperature for pure water would be 162 ± 5 K at 1Hz.

1483 The temperature dependence of the relaxation time for water between -20°C to +30°C [43] was

1484 found to follow the Fulcher equation

1485

1486 $$\tau(T) = A_F \exp\left(\frac{B_F}{T - T_0}\right)$$ (2.185)

1487

1488 with $A_F = 1.25\times10^{-13}$ s, $B_F = 669$ K, $T_0 = 138$ K. The extrapolated {1 Hz, 162 ± 5 K} datum

1489 agreed with the predicted Fulcher value {1 Hz, 162 K}. Given the large extrapolation over about

1490 11 orders of magnitude (!) this agreement constitutes good evidence that dielectric relaxation of

1491 water outside the first coordination shell of the Ca^{2+} and Li$^+$ cations is the same as pure water.

1492 This was supported by a similar extrapolation of LiCl in glycerol data that yielded a relaxation

1493 temperature equal to the directly observable value for pure glycerol at 1 Hz.

1494

1495 2.4   Conductivity Relaxation

1496 2.4.1   General Aspects

1497   As noted earlier, relaxation of polarization can occur either by translation of electric

1498 charge (electric current) or by dipole rotation/localized ion hopping (displacement current). Thus

1499 polarization induced by an electric field can occur by conductivity relaxation [44] arising from

1500 long range translational migration of point charges as well as by the dielectric relaxation

1501 considered so far. The time scale associated with a frequency invariant conductivity σ_0 is defined

1502 by (eq. 1.42)

1503

1504 $$\langle\tau_D\rangle = \sigma_0 / e_0 \varepsilon_\infty,$$ (2.186)

1505

1506 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

1507 ρ'' and M'' clearly indicate the time scale because they exhibit maxima in the frequency domain

1508 at $\omega \approx 1/\langle\tau_D\rangle$. The time constant τ_D in eq. (2.186) differs from the characteristic time τ_e in the

1509 Fermi gas expression for electronic conductivity in metals that is directly proportional to σ_0 [45]:

1510

1511 $$\tau_e = \frac{m}{ne^2}\sigma_0,$$ (2.187)

1512

1513 where n is the number density of charge carriers of effective mass m and charge e. The reason for

1514 the difference is that τ_e is the average time of travel between scattering events (collisions with

1515 ions, electrons, phonons or by umklapp), whereas τ_D is the residence time between (effectively

1516 instantaneous) jumps between adjacent sites. Nor is τ_D equal to τ_E for dielectric relaxation,

1517 although they are related by an expression that is derived below.

1518   Equation (2.186) implies that ionic conductivity cannot exceed ca. 10^3 Sm^{-1}, since τ_D

1519 cannot reasonably be less than a vibrational lifetime τ_v and ε_∞ is rarely greater than about 10.

1520 The vibrational lifetime is conveniently defined by the condition for critical damping (§1.11),

1521 $\omega_0 \tau_v = 1$, so that for a typical vibrational frequency of about $f \approx 10^{12}\,Hz \Rightarrow \omega \approx 6\times10^{12}\,rad/s$ the

1522 value of τ_v is about $2\times10^{-13}\,s$ and

1523

1524 $$\sigma_{0,max} \approx \frac{e_0 \varepsilon_\infty}{\tau_V} \approx \frac{\left(8.854\times10^{-12}\ F/m\right)(10)}{2\times10^{-13}\ s} \approx 450\ S/m, \qquad (2.188)$$

1525

1526 comparable with the highest conductivity observed for ionic conductors.

1527   The properties of the four basic functions for conductivity relaxation (eq. (2.106)) are

1528 conveniently illustrated using a circuit comprising three elements in series: (i) a capacitance

1529 $C_s = 10^{-6}\ F = 1\mu F$; (ii) a parallel combination of a resistance $R_1 = 10^8\ \Omega$ and capacitance

1530 $C_1 = 10^{-12}\ F(1pF)$ (iii) another parallel combination of a resistance $R_2 = 10^6\ \Omega$ and capacitance

1531 $C_1 = 10^{-12}\ F(1pF)$. The two parallel R_p-C_p elements could for example simulate crystal and inter-

1532 crystal impedances in a polycrystalline samples and the series capacitance C_s could simulate

1533 electrode polarization. As discussed below this circuit has been used by several groups and will

1534 be referred to as the "ideal" conductivity circuit.

1535   The electric modulus $M^* = M' + iM''$ is particularly useful for analyzing conductivity

1536 relaxation but it is controversial (a discussion of many of the issues is given in [1]). It was

1537 probably first defined by McCrum, Read and Williams [32], but its use in analyzing conductivity

1538 relaxation was initiated by Macedo and coworkers [44]. The usefulness of M* is illustrated by the

1539 simplest case of a constant conductivity σ_0 and constant relative permittivity ε_∞ (the reason for

1540 the subscripts will become clear when distribution functions are considered later). Consider the

1541 definitions

1542

1543 $$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \qquad (a),$$

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

(2.189)

1544

1545 Insertion of the relations $\varepsilon'' = \sigma_0 / e_0 \omega$ and $\varepsilon' = \varepsilon_\infty$ then yields

1546

1547
$$M' = \frac{1}{\varepsilon_\infty^D}\left(\frac{\omega^2\tau_D^2}{1+\omega^2\tau_D^2}\right) \tag{2.190}$$

1548
1549 and
1550

1551
$$M'' = \frac{1}{\varepsilon_\infty^D}\left(\frac{\omega\tau_D}{1+\omega^2\tau_D^2}\right). \tag{2.191}$$

1552

1553 Thus M" exhibits a desirable peak centered at $\omega_D = 1/\tau_D$ as a function of $\ln(\omega)$. The components

1554 of the complex resistivity ρ^* are related to those of M* by (eq. (2.106))

1555

1556
$$\rho' = \frac{M''}{e_0\omega} = \frac{\tau_D}{e_0\,\varepsilon_\infty^D}\left(\frac{1}{1+\omega^2\tau_D^2}\right) = \left(\frac{\rho_0}{1+\omega^2\tau_D^2}\right) \tag{2.192}$$

1557
1558 and
1559

1560
$$\rho'' = \frac{M'}{e_0\,\omega} = \frac{\tau_D}{e_0\,\varepsilon_\infty^D}\left(\frac{\omega\tau_D}{1+\omega^2\tau_D^2}\right) = \rho_0\left(\frac{\omega\tau_D}{1+\omega^2\tau_D^2}\right), \tag{2.193}$$

1561

1562 where $\rho_0 = 1/\sigma_0 = \tau_D/e_0\varepsilon_\infty^D$. The functions M" and ρ" have identical frequency dependencies

1563 but are weighted by $1/\varepsilon_\infty$ and ρ_0 respectively. The difference in weighting factors can be exploited

1564 to considerable advantage in the analysis of ac conductivity data (§2.3.5.6 - §2.3.5.8).

1565 For dielectric relaxation M* and ε^* are almost equivalent because a Debye peak in ε"

1566 also yields a Debye peak in M" [44] [see eqs. (2.132) and (2.133)]. The derivation of M* for a

1567 Debye dielectric without any conductivity is given in Appendix 2.1. It might appear that a peak in

1568 M" could be due to either a conductivity or dielectric process and that M* could not distinguish

1569 between them but this is not necessarily so because the average relaxation time $\langle\tau_D\rangle$ will be

1570 calculable from the limiting low frequency conductivity [eq. (2.73)] if the process is a

1571 conductivity relaxation, and the retardation time will not correlate with σ_0.if the peak in M" is

1572 due to a dielectric relaxation Also $\lim_{\omega\to 0} M'(\omega) = 1/\varepsilon_0$ for dielectric relaxation compared with

1573 $\lim_{\omega\to 0} M'_{conductivity}(\omega) = 0$ for conductivity relaxation. The archetypal example of dielectric

1574 relaxation being correlated with σ_0 occurs in the alkali silicate glasses and it was this correlation

1575 that originally led to the inference that the residual dielectric loss (after subtraction of $\sigma_0/e_0\omega$) is

1576 due to the same alkali migration process that produces σ_0 [27-31]. This led Macedo and

1577 collaborators [44] to first use M* in the analysis of conductivity relaxation.

1578 The low frequency conductivity relaxation limit for M ' is revealing because M ' is a

1579 measure of the restoring force in response to an electric field perturbation. The low frequency

1580 limit of this restoring force is finite for dielectric relaxation because the charge storage ability

1581   remains nonzero: $\lim\limits_{\omega\to\infty}\varepsilon'(\omega)=\varepsilon_0$. For conductivity relaxation the dielectric loss becomes infinite

1582   as $\omega\to 0$ (dissipation completely overrides any storage capability) and the restoring force is
1583   "short circuited". This is precisely analogous to the mechanical modulus going to zero as the
1584   viscosity of a viscoelastic material dominates at low frequency and the elasticity disappears. The
1585   electric modulus was first introduced to emphasize this mechanical analogy [32].
1586   An alternative to the electric modulus for analyzing materials in which the dielectric loss
1587   and conductivity are correlated has been proposed by Johari [46]. This proposal is similar in style
1588   to a mechanism for ionic conductivity proposed by Hodge and Angell [47] that was based on the
1589   one-dimensional Glarum diffusion model for dielectric relaxation [§1.12.6, Chapter One]. The
1590   Glarum model comprises a relaxing dipole that can relax either independently with retardation
1591   time τ_0 or by the arrival of a defect of some kind that relaxes it instantly. Hodge and Angell
1592   suggested that the dipole is a trapped ion/vacancy pair (known to exhibit Debye dielectric
1593   behavior, §2.3.1.2) and that the defects are itinerant ions that contribute to σ_0. Such diffusing
1594   ions would eliminate the dipole upon arriving by inserting themselves into the vacancy, consistent
1595   with the Glarum model. The average activation energy for oscillation of trapped ions and that for
1596   ion migration are presumed to be similar (perhaps identical), thus accounting for the nearly
1597   temperature invariant distribution of conductivity relaxation times. The Glarum function is
1598   mathematically similar to the Davidson-Cole function that has a (rarely observed) Debye-like low
1599   frequency loss. This low frequency behavior arises from the Glarum assumption that the dipole
1600   has just one retardation time. However if a distribution of dipole retardation times is assumed,
1601   corresponding to a distribution of sites in an amorphous material and/or local fields effects
1602   (§2.3.1.2) for example, better agreement with experiment might be obtained without changing the
1603   essential physics of the Glarum model.
1604
1605   2.4.2   Distribution of Conductivity Relaxation Times
1606   Both M^* and ρ^* can be formally described in terms of a distribution of conductivity
1607   relaxation times:
1608

1609
$$M^*(i\omega)=M_\infty\int_{-\infty}^{+\infty}g(\ln\tau_D)\left(\frac{i\omega\tau_E}{1+\omega^2\tau_D^2}\right)d\ln\tau_D \qquad (2.194)$$

1610

1611   and similarly for $\rho^*(i\omega)$. A distribution of conductivity relaxation times affects the dispersion

1612   of the corresponding complex admittance functions $\varepsilon^*(i\omega)$ and $\sigma^*(i\omega)$:

1613

1614
$$\sigma_0=\frac{\mathrm{e}_0\varepsilon_\infty^D}{\langle\tau_D\rangle}=\frac{\mathrm{e}_0}{M_\infty^D\langle\tau_D\rangle}, \qquad (2.195)$$

1615
$$\sigma_\infty=\mathrm{e}_0\varepsilon_\infty^D\left\langle\frac{1}{\tau_D}\right\rangle=\frac{\mathrm{e}_0}{M_\infty^D}\left\langle\frac{1}{\tau_D}\right\rangle, \qquad (2.196)$$

1616
1617   and

1618

1619 $$\varepsilon_0^D = \varepsilon_\infty^D \frac{\left\langle \tau_D^2 \right\rangle}{\left\langle \tau_D \right\rangle^2} \geq \varepsilon_\infty^D,$$ (2.197)

1620
1621 where the subscripts 0 and ∞ denote limiting low and high frequency limits respectively. Also, the
1622 commonly observed limiting high frequency power law behavior $\sigma'(\omega) \propto \omega^n (0 \leq n \leq 1)$ depends
1623 on the distribution: the broader the distribution the closer n is to unity. Values of n greater than
1624 unity imply that a resonance process occurs at higher frequencies (see below §2.4.3).
1625 A distribution of conductivity relaxation times is not easily distinguishable from dielectric
1626 and conductivity relaxations occurring together [36,44], although the dielectric relaxation will not
1627 be observable if $\tau_E \gg \tau_D$ because σ_0 will then exceed the limiting high frequency dielectric
1628 conductivity given by eq. (2.131):
1629

1630 $$\frac{\sigma'(\omega\tau_D \to 0)}{\sigma'_\mu(\omega\tau_E \to \infty)} = \frac{\sigma_0}{\sigma_\mu(\infty)} = \frac{\varepsilon_\infty}{\left\langle \tau_D \right\rangle}\left(\frac{\left\langle \tau_E \right\rangle}{\varepsilon_0 - \varepsilon_\infty}\right) = \frac{\varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty}\frac{\left\langle \tau_E \right\rangle}{\left\langle \tau_D \right\rangle} \gg 1.$$ (2.198)

1631
1632 This phenomenon has been directly observed in systems for which the dielectric retardation time
1633 is essentially constant but whose conductivity is increased by addition of electrolyte [48, 49] (also
1634 see §2.3.6.9 below).
1635
1636 ### 2.4.3 Contribution of Resonance Absorption
1637 If a resonance process occurs that is centered at a much higher frequency than
1638 $\omega_D = e_0\varepsilon_\infty / \sigma_0$ (eq. (2.186)) then the conductivity can increase more rapidly with frequency than
1639 the maximum proportionality to ω for a relaxation process. This is clear from the low frequency
1640 limit of eq. 1.395 in Chapter 1 for the resonance expression for the dielectric loss:
1641

1642 $$\varepsilon''(\omega) = \propto \omega$$ (2.199)

1643
1644 that implies a low frequency limit $\sigma_{resonance} \propto \omega^2$. This can yield a power law relation $\sigma \propto \omega^a$ for
1645 which $a > 1$.
1646
1647 ### 2.4.4 Constant Phase Element Analysis
1648 It is sometimes useful to have a circuit element for which the phase angle is independent
1649 of ω,
1650

1651 $$W^*(i\omega) = W(\omega)\exp\left(\frac{\pm i\,\alpha\pi}{2}\right),$$ (2.200)

1652
1653 where $W(\omega)$ is any real function and $0 < \alpha \leq 1$ is also real (the positive sign in the exponent
1654 corresponds to an admittance and the negative sign to an impedance). However as noted in
1655 Chapter One and §2.4.3 eq. (2.200) can only be valid over a restricted frequency range because

1656 otherwise the underlying distribution of relaxation/retardation times cannot be normalized.
1657 Equation (2.200) is a generalization of the Warburg impedance for which $\alpha = 0.5$.
1658
1659 ## 2.4.5 Estimation of σ_0

1660 Several methods have been published for estimating σ_0 in situations where it has been
1661 contaminated by such factors as electrode polarization and intergranular impedances. An accurate
1662 value for σ_0 is often important because, in addition to the obvious need for reliable data, its
1663 contribution to ε'' must be subtracted for permittivity analyses (the attendant difficulties have
1664 been discussed by Ravaine and Souquet [52, 53]). Accurate values of σ_0 are also needed in order
1665 to determine reliable activation energies for conductivity. For example if $\log(\sigma)$ measured at
1666 constant measuring frequency ω_{meas} is plotted against $1/T$ in the usual Arrhenius fashion then
1667 spurious changes in slope can result from both electrode polarization and bulk relaxation effects.
1668 (1) If the measuring frequency ω_{meas} is so low that polarization is significant then the
1669 measured conductivity will be less than σ_0, by an amount that increases with increasing
1670 temperature because of the shift to higher frequencies of the polarization σ' spectrum (which has
1671 essentially the same effective activation energy as the sample conductivity).
1672 (2) A fictitiously low activation energy is then obtained at high temperatures as ω_{meas} probes
1673 deeper into the polarization relaxation. A spuriously low activation energy can also occur at low
1674 temperatures when ω_{meas} lies within the bulk relaxation frequency range where σ' is often
1675 observed to increase as $\omega^\alpha \left(\alpha < 1 \right)$. In this case the measured conductivity will exceed σ_0 by an
1676 amount that decreases with increasing temperature and the measured activation energy will be
1677 smaller than the true value by the factor $\alpha = d\ln\sigma' / d\ln\omega$:
1678

1679 $$E_{a,obs} = E_{a,true}\left(1 - \alpha\right). \tag{2.201}$$

1680
1681 In cases where $\alpha \approx 1$, as occurs in some electronic semiconductors [48], the fixed frequency
1682 conductivity is therefore almost independent of temperature in the bulk relaxation temperature
1683 region.
1684
1685 ### 2.4.5.1 Analyses in the Complex Resistivity Plane

1686 Ravaine and Souquet [52,53] used the complex resistivity plane for determining σ_0 of
1687 alkali silicate glasses in the presence of electrode polarization using low frequency extrapolations
1688 to the real axis. They fitted the high frequency spectrum (i.e. sample relaxation) to the Cole-Cole
1689 [54] function (§1.12.5) and extrapolated the Cole-Cole semicircle to the real axis. For severe
1690 polarization Armstrong et al. [55-59] used a similar method based on extrapolation of the high
1691 frequency polarization spike to the real axis. This method is restricted to high conductivities
1692 whose relaxation frequency lies above the measuring frequency range.
1693
1694 ### 2.4.5.2 Modulus and Resistivity Spectra

1695 In cases where electrode polarization and conductivity relaxations overlap significantly

1696 and no plateau in σ' is observed, σ_0 can be estimated from eq. (2.186) if $\langle \tau_D \rangle$ and ε_∞ are known.

1697 These can sometimes be determined with sufficient precision by fitting $M''(\omega)$ to an appropriate

1698 empirical function because M'' is insensitive to high capacitance effects such as electrode

1699 polarization and intergranular impedances so that only the bulk relaxation is included in the fitted

1700 function. For this application the fit to M'' should preferably be weighted by the lower frequency

1701 data because these reflect the longer relaxation time components of the distribution that contribute

1702 more significantly to $\langle \tau_D \rangle$. The maximum in ρ'', ρ''_{max}, can also be used to estimate σ_0 to within

1703 about 10% if the full width at half height of the peak in ρ'' (Δ decades) can be determined:

1704

1705 $$\sigma_0 \approx \frac{1}{1.75 \Delta \rho''_{max}}.$$ (2.202)

1706

1707 If only the maximum in ρ'' at ω_{max} is observable σ_0 can still be estimated from the value of ρ'

1708 at ω_{max} by assuming $\rho''(\ln \omega)$ to be symmetric:

1709

1710 $$\sigma_0 \approx \frac{1}{2 \rho'(\omega_{max})}.$$ (2.203)

1711

1712 2.4.5.3 Complex Admittance Plane

1713   One of the first applications of complex plane plots was to polycrystalline yttria-zirconia

1714 electrolytes by Bauerle [60]. Bauerle gave an excellent discussion of equivalent circuits and their

1715 corresponding complex admittance plane plots, but the only circuit used in their data analysis was

1716 a series combination of two parallel R_pC_p elements and a series resistance R_s. The first parallel

1717 R_pC_p element in this circuit represented the electrode interface: the capacitance of a double layer

1718 in parallel with the resistance of an oxygen gas-oxide ion charge transfer process. The second

1719 R_pC_p element represented an intergranular boundary ("constriction") impedance, and the pure

1720 resistance simulated the bulk crystal. The experimentally observed complex admittance plane

1721 plots were in excellent agreement with the equivalent circuit predictions. The zero frequency

1722 conductivity predicted from the complex plane plot was also in excellent agreement with four

1723 terminal data, and the expected dependence of the electrode impedance on oxygen partial pressure

1724 was observed. Despite these successes, some disadvantages of the method should be pointed out.

1725 First, in assuming that the bulk crystal acts as a pure resistance the analysis implicitly assumes

1726 that the measuring frequencies are well below the conductivity relaxation frequency, that can only

1727 be confirmed retrospectively. Second, although there are three relaxing elements (since the

1728 sample resistance must realistically have a capacitance in parallel with it), the complex admittance

1729 plane exhibits only two arcs that reflect the differences between the relaxing elements. If the

1730 observed relaxations overlap significantly, an assumption must be made about the shapes of the

1731 two relaxations before extrapolations are made, i.e. a functional form for the extrapolating

1732 function must be chosen. Bauerle's data were well described by the Cole-Cole function but this

1733 would not be expected to occur in general.

1734

1735   2.4.6   Examples

1736   2.4.6.1 Electrode Polarization and Bulk Relaxation in the Frequency Domain

1737   Consider an "ideal" equivalent circuit similar to that used by Bauerle except that the series

1738   resistance is replaced by a series capacitance, with specific values of the parallel R_pC_p elements

1739   being $\left[R_1 = 10^8\,\Omega, C_1 = 10^{-11}\,\text{F} \Rightarrow \tau_1 = R_1C_1 = 10^{-3}\,\text{s} \right]$, $\left[R_2 = 10^6\,\Omega, C_2 = 10^{-11}\,\text{F} \Rightarrow \tau_2 = R_2C_2 = 10^{-5}\,\text{s} \right]$

1740   and $\left[C_s = 10^{-6}\,\text{F} \right]$. The distribution of conductivity relaxation times then comprises two delta

1741   functions at $\tau_1 = 10^{-3}$ s and $\tau_2 = 10^{-5}$ s. The shorter relaxation time element simulates the crystal

1742   impedance in a polycrystalline preparation, the longer relaxation time element simulates an

1743   intergranular impedance, and the series capacitance simulates electrode polarization. This circuit

1744   has been found to be useful in analyzing the electric response of a variety of conducting materials,

1745   including a superionic conductor [61], an electronic semiconductor [62], and a normal ionic

1746   conductor [9]. The relaxation time averages are

1747

1748 $$\left\langle \tau_D^2 \right\rangle = \frac{\tau_1^2 + \tau_2^2}{2} = 5.0005 \times 10^{-9}\ \text{s} \tag{2.204}$$

1749 $$\left\langle \tau_D \right\rangle = \frac{\tau_1 + \tau_2}{2} = 5.05 \times 10^{-5}\ \text{s} \tag{2.205}$$

1750 $$\left\langle \tau_D^{-1} \right\rangle = \frac{\tau_1^{-1} + \tau_2^{-1}}{2} = 5.05 \times 10^{+5}\ \text{s} \tag{2.206}$$

1751

1752   The high frequency relative permittivity is (assuming k = 1 for convenience so that $C_0 = e_0$

1753   numerically)

1754

1755 $$\varepsilon_\infty = \frac{C_1 C_2}{e_0 (C_1 + C_2)} = 5.647, \tag{2.207}$$

1756

1757   and the low frequency relative permittivity is

1758

1759 $$\varepsilon_0 = \varepsilon_\infty \frac{\left\langle \tau_D^2 \right\rangle}{\left\langle \tau_D \right\rangle^2} = (5.647) \frac{\left(5.005 \times 10^{-9}\right)}{\left(5.05 \times 10^{-5}\right)^2} = 11.083. \tag{2.208}$$

1760

1761   The limiting low and high frequency conductivities are

1762

1763 $$\sigma_0 = \frac{\epsilon_0 \varepsilon_\infty}{\left\langle \tau_D \right\rangle} = \frac{\left(8.854 \times 10^{-12}\right)(5.647)}{\left(5.05 \times 10^{-5}\right)} = 9.9 \times 10^{-7}\ \text{S m}^{-1} \tag{2.209}$$

1764 $$\sigma_\infty = \epsilon_0 \varepsilon_\infty \left\langle 1/\tau_D \right\rangle = \left(8.854 \times 10^{-12}\right)(5.647)\left(5.05 \times 10^{+5}\right) = 2.53 \times 10^{-5}\ \text{S m}^{-1}. \tag{2.210}$$

1765

1766   (1)   The ρ'' and M'' spectra both exhibit two peaks the heights of which reflect the different

1767   weighting of the two functions - eqs. (2.191) and (2.193). The two ρ" peak heights differ by the

1768   ratio of the resistances $10^8/10^6 = 10^2$, whereas the M" peaks are equal in height because the two

1769   capacitances are equal. If the capacitances were different and the resistances the same then the

1770   peaks in ρ" would have the same height and those in M" would differ. Also ρ" increases

1771   indefinitely at low frequencies due to C_s whereas M" is unaffected.

1772   (2)   After subtraction of the contribution of σ_0 to ε", and of the limiting high frequency

1773   contribution of ε_∞ to σ", both σ" and ε" exhibit a single peak at a frequency between the two

1774   maxima exhibited in the M" and ρ" spectra. These single peaks in the admittance functions occur

1775   because at intermediate frequencies the high frequency RC element behaves as a resistance and

1776   the low frequency RC element behaves as a capacitance. As noted in §2.2.4 the effectively series

1777   RC circuit will produce just a single loss peak in the admittance. For the electrode polarization

1778   relaxation caused by C_s in series with the sample resistance $\left(R_1 + R_2\right)$ peaks in $\sigma" - e_0 \varepsilon_\infty \omega$ and

1779 $\varepsilon" - \sigma_0/e_0\omega$ are observed at lower frequencies.

1780   (3)   A low frequency decrease in σ' and increases in ε' and ρ" are found that are due to the

1781   electrode polarization simulated by C_s. For expositional clarity the value of C_s was chosen to

1782   ensure a clean separation between the simulated polarization and bulk relaxations but this does

1783   not occur in typical experimental data.

1784   (4)   The complex plane plots have both advantages and disadvantages compared with the

1785   spectra. Two disadvantages are the inconvenience of locating the frequencies of maximum loss,

1786   and of comparing these frequencies in M* and $\rho*$ plots because of the opposite directions of

1787   increasing frequency. On the other hand, complex plane plots are useful for extrapolations. For

1788   example in highly conducting materials whose conductivity relaxation frequency $1/\langle\tau_D\rangle$ lies

1789   above the measuring frequency, and for which electrode polarization is significant or even severe,

1790   the polarization spike in the $\rho*$ plane can be extrapolated to the real axis to give an estimate of

1791 $\sigma_0 = 1/\rho_0$. At frequencies above the conductivity relaxation frequency, σ_0 is manifested as a

1792   spike in the $\varepsilon*$ plane, corresponding to the limiting values of $\lim_{\omega\to0}\varepsilon" = \lim_{\omega\to0}\sigma_0/\epsilon_0\omega = \infty$ and

1793 $\lim_{\omega\to0}\varepsilon' = \varepsilon_0$.

1794

1795   2.4.6.2 Conductivity Relaxation in Sodium β – Alumina

1796   Permittivity, modulus and resistivity spectra of single crystal sodium β -alumina at 113 K

1797   have been reported by Grant and Ingram [64,65]:

1798   (i)   the ε" spectrum measured in the direction perpendicular to the conduction planes;

1799   (ii)   the M" spectra in orientations perpendicular and parallel to the conducting planes;

1800   (iii)   the Z" spectrum measured in the direction of the conduction planes.

1801   The frequency of maximum Z" in the parallel orientation was close to the frequency of

1802   maxima in M" and ε" measured in the perpendicular orientation, and the activation energy for the

1803   parallel resistivity spectrum was close to that for the perpendicular dielectric loss spectrum. The

1804   data for the perpendicular orientation were interpreted in terms of a Maxwell layered dielectric

1805   [65], with each insulating spinel block being a capacitance and each conduction plane a

1806   resistance. The activation energy for the dielectric loss was thus determined by that of the

1807 conductivity of the conducting layers, that the data suggest is similar in directions parallel and
1808 perpendicular to the conduction planes. An extraordinarily large width of the M" spectrum for
1809 single crystal Na β – alumina was observed in the parallel orientation [66,67], indicating a very
1810 broad distribution of conductivity relaxation times: the resistivity and modulus spectra taken
1811 together suggested that the distribution was bimodal. Grant and Ingram proposed that at 113 K the
1812 low frequency conductivity is determined by an activated localized ion motion that is the same in
1813 both orientations. The higher frequency conductivity, which contributed to M" but not to ρ",
1814 resulted from a relatively free motion of ions crossing low energy barriers. These processes were
1815 consistent with low temperature localization of sodium ions deduced from NMR data [68].
1816 Localized activation is not the rate determining step at high temperatures and the well-established
1817 low activation energy for conductivity in sodium β-alumina was observed. Spectra of M" and Z"
1818 for a representative polycrystalline specimen at 113 K were also reorted. The Z" spectrum was
1819 uninformative at this temperature, increasing monotonically at low frequencies due to electrode
1820 polarization. The M" spectrum exhibited a maximum at about the same frequency as the single
1821 crystal M" spectrum observed perpendicular to the conduction planes, and a reproducible shoulder
1822 was observed at about the same frequency as M" observed parallel to the conduction planes in
1823 single crystals.
1824 This work demonstrates that comparison of the functions M", ρ" and ε" can uncover
1825 details of the conductivity behavior of sodium β – alumina that could not even be discussed if
1826 only σ^* and ε^* data were used.
1827
1828 2.4.6.3 Complex Impedance Plane Analysis of Electrode Polarization in Sintered β –
1829 Alumina.
1830 The use of the complex impedance plane for extrapolating polarization phenomena to
1831 obtain data on the bulk material was used extensively by Armstrong and coworkers in their
1832 studies of superionic conductors such as Na β-alumina [55] and Ag-Rb iodide [54-58]. A spike
1833 in the complex impedance plane corresponds to the low frequency increase in Z" due to the series
1834 electrode capacitance and extrapolation of this spike to the real axis yielded the limiting low
1835 frequency values of Z' and therefore of ρ_0. Different surface preparations were observed to
1836 affect the measured impedance but all of the extrapolations gave the same values for ρ_0. This
1837 method is clearly most appropriate for very highly conducting materials whose conductivity
1838 relaxation lies at frequencies well above those used experimentally.
1839
1840 2.4.6.4 Complex Impedance Plane Analysis of Atmosphere Dependent Electrode Effects in KHF_2
1841 Complex impedance plane analysis was also used by Bruinink and Broers [69] for the α
1842 and β phases of KHF_2. In an atmosphere of hydrogen with platinum paint electrodes, the complex
1843 impedance plane plot of data for α-KHF_2 was consistent with a Warburg impedance in parallel
1844 with the bulk resistance and capacitance [69], and extrapolation to the real axis gave a value of
1845 ρ_0 in agreement with a separately determined four terminal dc value. This plot gave no indication
1846 of interfacial polarization, consistent with α-KHF_2 being a proton conductor and the platinum
1847 paint electrodes behaving as reversible hydrogen electrodes. This contrasted sharply with the low
1848 frequency behavior of α-KHF_2 in a vacuum, where a double layer capacitance of about 440 mF
1849 m^{-2} per electrode in parallel with a Faradaic resistance of about $2\times10^4\,\Omega$m per electrode

1850 produced an additional semicircle in the complex plane. For the polycrystalline β-phase the
1851 complex plane plot was essentially unchanged for data taken in both a hydrogen atmosphere and a
1852 vacuum [69] and is consistent with a Warburg impedance in series with a parallel RC element,
1853 corresponding to electrode polarization due to blocking of K^+ and/or F^- charge carriers. An *RC*
1854 transmission line was used to rationalize the Warburg impedance in terms of bulk electrical
1855 relaxation.
1856
1857 2.4.6.5 Intergranular Effects in Polycrystalline Electrolytes
1858 The effects of intergranular material on the overall electrical response of polycrystalline
1859 electrolytes have been extensively documented. Only one example is discussed here [9,66]. The
1860 simplest equivalent circuit representation of such materials comprises two parallel *RC* elements
1861 in series, where one element is associated with a crystallite and the other with intergranular
1862 material. Armstrong et al. [70] showed that such a series circuit can represent the principle
1863 features of polycrystalline electrolytes. Since the interface is thin and the permittivities of ionic
1864 solids typically vary by a factor of less than 10, the capacitance C_i associated with the interface is
1865 much higher than that of the grain C_p:
1866

1867 $$C_i = \frac{\epsilon_0 \, \varepsilon' A_i}{d_i} \gg \epsilon_0 \varepsilon' = k \, C_p \qquad\qquad (2.211)$$

1868
1869 where A_i is the average cross section area, d_i is the average thickness of the intergranular material,
1870 and $k = e_0 / C_0$ is the cell constant.
1871
1872 2.4.6.6 Intergranular Cracking
1873 Experimental M'' and ρ'' spectra for a polycrystalline material known to have
1874 intergranular cracking were reported in [9]. The spectra were similar to those for two parallel
1875 $R_p C_p$ elements in series although the experimental peaks were broader - they could be
1876 approximated as the sum of two Debye peaks of equal heights separated by about a decade in
1877 frequency, so that the maxima in Z'' and M'' could be approximated as $R_p / 4$ and $C_0/4C_p$,
1878 respectively. Computed values of R and C for the intergranular and granular material in the
1879 cracked sample, using these approximations and assuming a resolution into symmetric ρ'' peaks,
1880 were:
1881
1882 Lower Frequency (Intergranular) Relaxation in Cracked Sample

1883 $$\tau_i = \frac{1}{\omega_{\max(Z'')}} = 6.4 \times 10^{-6} \text{ s}, \qquad\qquad (2.212)$$

1884 $$R_i \approx 4Z''_{\max} = 6.4 \times 10^6 \, \Omega, \qquad\qquad (2.213)$$

1885 $$C_i = \frac{\tau_i}{R_i} \approx 1.0 \, \text{pF}. \qquad\qquad (2.214)$$

1886

1887   Higher frequency (Intragranular) Relaxation in Cracked Sample

1888 $$\tau_c = \frac{1}{\omega_{max(Z'')}} = 1.6 \times 10^{-7} \text{ s},\tag{2.215}$$

1889 $$R_c \approx 4Z''_{max} = 2.6 \times 10^6 \, \Omega,\tag{2.216}$$

1890 $$C_c = \frac{\tau_c}{R_c} \approx 0.06 \, \text{pF}\tag{2.217}$$

1891
1892   The impedance spectrum was drastically altered after the intergranular cracking had been
1893   annealed out [9]. A single peak in Z'' was observed in the annealed sample that was essentially
1894   indistinguishable from the high frequency peak in the cracked material, strongly suggesting that it
1895   was due to intra-crystal relaxation and that the additional low frequency peak for the cracked
1896   sample was due to thin air gaps. Consistent with this, the modulus spectrum was essentially
1897   unchanged by annealing since it was unaffected by the high capacitance cracks. The estimates of
1898   the intragranular and intergranular resistances were confirmed by the σ_0 data: the observed
1899   conductivity of the cracked sample was largely determined by the intergranular resistance, and the
1900   ratio of the conductivities of the sample before and after annealing should have been
1901

1902 $$\frac{Z''^{low\,\omega}_{max} + Z''^{high\,\omega}_{max}}{Z''^{high\,\omega}_{max}} = \frac{2.25 \times 10^6}{0.65 \times 10^6} = 3.5,\tag{2.218}$$

1903
1904   in fair agreement with
1905

1906 $$\frac{\sigma_{annealed}}{\sigma_{cracked}} = 3.1.\tag{2.219}$$

1907
1908   The combination of modulus and impedance spectroscopies once again revealed details that could
1909   not be obtained from the original σ' and ε' data.
1910
1911   2.4.6.7 Intergranular Gas Adsorption
1912   The effects of oxygen and alkali doping on the electrical response of polycrystalline zinc
1913   oxide were studied by Seitz and Sokoly [71]. Only the effects of oxygen pressure are discussed
1914   here. An increase in conductivity was observed with decreasing oxygen pressure and the absence
1915   of changes due to different electrode materials implied that adsorbed oxygen at grain surfaces was
1916   responsible for the observed polarization of the sample. The conductivity and permittivity were
1917   plotted explicitly as a function of frequency and these data allowed M'' and ρ'' spectra to be
1918   calculated without difficulty (unpublished results obtained by the present author). The calculated
1919   M'' and ρ'' spectra exhibited two partially resolved peaks whose estimated magnitudes were
1920   consistent with a thin high capacitance - high resistance layer determining the low frequency
1921   response. Both peaks in the M'' spectrum had comparable half widths (ca. 1.5 decades) and their
1922   relative maximum values 8×10^{-4} and 1.1×10^{-2} (ratio 14) were a good (inverse) measure of the
1923   relative capacitance of each relaxation: $C_\ell / C_h \approx 13$. The resistance ratio R_ℓ / R_h of the low

1924   frequency high frequency relaxation could then be estimated from the two values of f_{max} (ca.

1925 5×10^2 and 3×10^5 Hz) to be about 45:

1926

1927
$$\frac{R_\ell C_\ell}{R_h C_h} \approx 600 \approx \frac{13 R_\ell}{R_h} \Rightarrow \frac{R_\ell}{R_h} \approx 45 .$$
(2.220)

1928

1929   The conductivity estimated from the height of the lower frequency resistivity peak was 1.1×10^{-7}

1930   S m^{-1}, in reasonable agreement with the low frequency plateau value of 1.3×10^{-7} S/m. From the

1931   relative frequencies of the M" maxima and the relative heights of the (partly resolved) ρ" maxima,

1932   the conductivity of the high frequency relaxation was estimated to be about $10^{-6 \pm 1}$ S m^{-1}. Because

1933   of its higher associated capacitance the lower frequency relaxation almost certainly corresponded

1934   to an intergranular impedance, and its removal by a reduction in oxygen pressure should therefore

1935   have increased the sample conductivity by about 45 but have a small effect on the measured

1936   permittivity (since removal of a high series capacitance has little effect on the total impedance).

1937   This predicted change in resistivity agreed with the qualitative statement that conductivity

1938   increased with decreasing oxygen pressure [71].

1939

1940

1941   Appendices

1942

1943   Appendix 2.1 Derivation of M* for a Debye Relaxation with No Additional Separate
1944   Conductivity
1945   These derivations are shown for pedagogical clarity rather than mathematical elegance.

1946   (1) $\Delta\varepsilon \equiv \varepsilon_0^E - \varepsilon_\infty^E; \tau_D = \left(\varepsilon_\infty^E / \varepsilon_0^E\right)\tau_E; M_0^E = 1/\varepsilon_0^E; M_\infty^E = 1/\varepsilon_\infty^E$

1947   (2) $M* = 1/\varepsilon* \Rightarrow M' = \dfrac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}; M'' = \dfrac{-\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}$

1948   (3) $\varepsilon' = \varepsilon_\infty^E + \dfrac{\left(\varepsilon_0^E - \varepsilon_\infty^E\right)}{1 + \omega^2\tau_E^2} = \varepsilon_\infty^E + \dfrac{\Delta\varepsilon}{1 + \omega^2\tau_E^2}; \varepsilon'' = \dfrac{\Delta\varepsilon\omega\tau_E}{1 + \omega^2\tau_E^2}$

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

1949

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

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

1950   (4)
$$= \frac{1}{\varepsilon_0^E} + \frac{\varepsilon_\infty^E\omega^2\tau_E^2 - \dfrac{\varepsilon_\infty^2}{\varepsilon_0}\omega^2\tau_E^2}{\left(\varepsilon_0^E\right)^2\left(1 + \dfrac{\left(\varepsilon_\infty^E\right)^2}{\left(\varepsilon_0^E\right)^2}\omega^2\tau_E^2\right)} = \frac{1}{\varepsilon_0^E} + \frac{\dfrac{\varepsilon_\infty^E}{\left(\varepsilon_0^E\right)^2}\omega^2\tau_E^2 - \dfrac{\left(\varepsilon_\infty^E\right)^2}{\left(\varepsilon_0^E\right)^3}\omega^2\tau_E^2}{\left(1 + \dfrac{\left(\varepsilon_\infty^E\right)^2}{\left(\varepsilon_0^E\right)^2}\omega^2\tau_E^2\right)} = \frac{1}{\varepsilon_0^E} + \frac{\left(\dfrac{1}{\varepsilon_\infty^E} - \dfrac{1}{\varepsilon_0^E}\right)\dfrac{\left(\varepsilon_\infty^E\right)^2}{\left(\varepsilon_0^E\right)^2}\omega^2\tau_E^2}{\left(1 + \dfrac{\left(\varepsilon_\infty^E\right)^2}{\left(\varepsilon_0^E\right)^2}\omega^2\tau_E^2\right)}$$

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

1951

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

1952   (5)

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

1953
1954   A Matlab®/Octave program for computing the components of M* with added conductivity is
1955   given below in Appendix 2.2.
1956

1957
1958   Appendix 2.2 Matlab®/GNU Octave Codes
1959   Computation Code for a Debye Relaxation with Additional Separate Conductivity σ_0.
1960   The algebraic derivation is excessively tedious and is replaced here by a
1961   Matlab®/GNUOctave code that plots both components of the $\varepsilon*$ and M* functions. The values
1962   of the input parameters are entered by editing the m-file.
1963
1964   % FUNCTION DebyeCondM Computes and Plots M* for Debye E* plus constant conductivity
1965   function HD = DebyeCondM
1966   w = logspace(-6,+6,1200);
1967   Logw = log10(w);
1968   E00   = 8.854E-12;   % Vacuum permittivity in F/m
1969   E0D   = 20;   % Low f dielectric relative permittivity
1970   EinfD = 10;   % High f dielectric relative permittivity
1971   DelE = E0D - EinfD;   % Dielectric dispersion range
1972   EinfE = 3;   % High f conductivity relative permittivity
1973   TauD = 10^-4   % Dielectric relaxation time
1974   Sigma0 = 10^-15;   % Conductivity in S/m
1975   Tausig = E00*EinfE/Sigma0 % Conductivity relaxation time
1976   E2sig = Sigma0./(E00*w);   % Conductivity contribution to E2
1977   % CALCULATE E1 and E2
1978   wTauD = w*TauD;
1979   Num = 1./(1 + wTauD.^2);
1980   E1 = EinfD + DelE*Num;   %Debye E1
1981   E2 = DelE*wTauD.*Num + E2sig; % Debye E2 + Conductivity E2
1982   Denom = E1.^2 + E2.^2;
1983   M1 = E1./Denom;
1984   M2 = E2./Denom;
1985   subplot (2,2,1);
1986   plot (Logw, E1);
1987   ylabel("E1");
1988   subplot (2,2,2);
1989   plot (Logw, E2);
1990   ylabel("E2");
1991   subplot (2,2,3);
1992   plot (Logw, M1);
1993   ylabel("M1");
1994   subplot (2,2,4);
1995   plot (Logw, M2);
1996   ylabel("M2");
1997
1998   return
1999

2000
2001   Appendix 2.3 Derivation of Debye Dielectric Expression from Equivalent Circuit
2002   Impedance of $R_s + C_s$ is

2003 $$Z_s = R_s + 1/i\omega C_s = \left(1+i\omega R_s C_s\right)/i\omega C_s = \left(1+i\omega\tau_s\right)/i\omega C_s \qquad (C1)$$

2004   and its admittance is

2005 $$A_s = 1/Z_s = i\omega C_s /\left(1+i\omega\tau_s\right) \qquad (C2)$$

2006   where $\tau_s \equiv R_s C_s$. The total admittance is

2007 $$A^* = i\omega C_s /\left(1+i\omega\tau_s\right) + G_p + 1/\left(i\omega C_p\right) \qquad (C3)$$

2008   and the complex capacitance is

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

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

2009 $$= \frac{\left[C_p\left(1+\omega^2\tau_s^2\right)+C_s\left(1-i\omega\tau_s\right)\right]}{1+\omega^2\tau_s^2} - \frac{iG_p}{\omega} \qquad (C4)$$

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

2010   from which eqs. (2.157) and (2.158) obtain.
2011

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