Journal of Physics and Chemistry of Solids 70 (2009) 546–554

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Comments on the electric modulus formalism model and superior alternatives to it for the analysis of the frequency response of ionic conductors

J. Ross Macdonald *

Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255, USA

ARTICLE INFO

Article history:
Received 9 August 2008
Received in revised form
13 November 2008
Accepted 7 December 2008

Keywords:
A. Amorphous materials
A. Glasses
D. Dielectric properties
D. Electrical properties
D. Transport properties

ABSTRACT

Because of the past and continuing wide usage of the 1973 original modulus formalism (OMF) model for analyzing dispersive frequency-response data of ion-conducting materials, it is important to discuss and demonstrate its theoretical and experimental inadequacies to help avoid its future use and to describe and illustrate important alternatives to it. The OMF fits data with a K1 response model alone, one indirectly derived from stretched-exponential temporal behavior, while the corrected modulus formalism (CMF) involves the composite CK1 model, one that includes in addition a separate free, parallel bulk dielectric parameter, $\varepsilon_{D\infty}$. The crucial error of the OMF approach is its identification of a high-frequency-limiting dielectric constant intrinsic to K1 response and associated entirely with conductive effects, with the full high-frequency-limiting dielectric constant of the material, ε_{∞}, one that must include the non-ionic, primarily dipolar quantity $\varepsilon_{D\infty}$. Comparison here of OMF fitting results with those of the CMF CK1 model for both an experimental data set and an exact one derived from it demonstrate the incorrectness of the OMF and the virtues of the CK1 alternative. The OMF fitting approach, but not the CMF one, leads to crucial inconsistency between the estimates of its β shape parameter for fits of the data expressed at all immittance levels except those of σ' and ε'', where it yields the same results as the CK1. Its incorrect β estimates, extensively used in the Ngai coupling model and interpreted as being associated with ion–ion correlations, also lead to erroneous "excess wing" effects in plots of the imaginary part of the data and fit at the modulus level. Further, OMF modulus-level fits yield non-physical estimated values of the characteristic relaxation time of the K1 model. Finally, some possible alternatives to the CK1 model are discussed for situations involving dielectric-system dispersion.

1. Introduction

The present subject is important because it deals with gaining understanding of the frequency response of ion-conducting materials of practical value, and because it discusses and corrects an incorrect fitting model for it originally proposed in 1973, the Mohnihan modulus formalism [1]. This model has been so widely employed since then that as many as a thousand or more published papers, many by Ngai and co-authors, have used this approach for the analysis of conductive-system frequency-response data. Note that the electric modulus, $M(\omega)$, is a dimensionless complex quantity and is the inverse of the relative permittivity, $\varepsilon(\omega)$. A list of acronym and fitting model definitions is included below.

In a paper published in 2000, 17 references were cited in support of the wide practice of the original modulus formalism (OMF) [2]. Nevertheless, the OMF model is wrong, and thus all results and physical conclusions based on its application are correspondingly incorrect. How is it possible that such an endemic but erroneous model, one that has virtually become the standard fitting approach, can continue to be so widely used, especially for the more than 14 years since it was shown to be erroneous [see Refs. [3–6] and references therein]? A main cause is that the originators and subsequent users of the OMF since 1994 have never discussed these previously published reasons for its failure in any of their publications, including two recent ones in which they responded to criticisms of the modulus formalism [7,8]. Had these responses discussed the earlier criticisms of the OMF cited above, their authors would have needed to accept or disprove the identification of errors in it. That they have done neither suggests that they were unable to counter the errors so identified.

* Tel.: +1 919 967 5005.
E-mail address: macd@email.unc.edu

0022-3697/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2008.12.012

Nomenclature

C	a capacitance or dielectric constant in parallel with part of a composite model
CK1S	K1 model with a capacitance C (representing $\varepsilon_{D\infty}$) in parallel with it and a constant-phase function in series with the combination
CMF	corrected modulus formalism: e.g., the CK1 fitting model
CNLS	complex nonlinear least-squares fitting of data
CSD	conductive-system dispersion involving mobile charges
CUNS	the CK1S model with β_1 fixed at the value of 1/3
DCk	Davidson–Cole models for $k = D$ and 0
DRT	distribution of relaxation times
DSD	dielectric-system dispersion involving dipoles
k	k = D: DSD model; $k = 0$: usual CSD model; $k = 1$: transformed CSD model
K*k*	Kohlrausch stretched-exponential fitting models for $k = D$, 0, and 1
LEVM	the name of a CNLS fitting program (Ref. [20])
OMF	original modulus formalism: the K1 model without a parallel C
PDRMS	RMS value of the RSD values of all the free parameters of a fit
PWT, UWT	proportional weighting for a CNLS fit or unity weighting
R	a resistor in parallel with part of a composite model
RCKDS	composite model with R and C in parallel with the DSD KD model and the result in series with a constant-phase element
RSD	relative standard deviation of an estimated parameter value

In Ref. [7] of 2003, its authors addressed "conflicting points of view" that "demonstrate the diversity of ideas in research on the dynamics of ions," but unfortunately, they ignored all prior published work of the present author that showed the OMF incorrect, certainly a conflicting point of view! Later, in 2005 Ref. [8], entitled "Comments on the electric modulus function," was devoted to presenting arguments in favor of the OMF and correcting "several misunderstandings and misrepresentations" of it. Again, no mention was made, however, of either theoretical or experimental facts that prove the OMF to be not just inadequate but incorrect.

Nearly all the authors (but see note in Ref. [8] listing) of the above publications supporting and justifying the OMF were aware of the earlier work that identified its failures and discussed valid alternatives to it, yet they ignored them. Science is based on a system of checks and balances and is diminished when checks are ignored. It is, of course, insufficient to just show that some idea or model is wrong; one needs to demonstrate valid alternatives. This has been done and led to an apparently minor yet crucial change in the interpretation of the OMF and to alternatives to its use for fitting and interpreting immittance data [3–6]. The result has been termed the corrected modulus formalism (CMF). Demonstration and discussion of the failure of the OMF and of the strengths of the CMF are summarized later herein.

An example of the entrenched and continuing support of the OMF is a recent negative comment of a reviewer who said, the OMF and CMF "are just different representations of the data, and no physics (is) at stake." The actual situation is that the OMF is a theoretically invalid model which leads to inconsistent data-fitting results; the CMF is a valid model that usually provides the best fit of experimental data compared to that of other models; and the interpretation of the physics implicit in the OMF is wrong and that in the CMF is correct! Had this reviewer's assessment been in fact correct, work pointing out the failure of the OMF and reasons for replacing it by the CMF would not have resulted in earlier published papers. Such ignorance, probably closely allied to the continuing failure of OMF supporters and users to cite contrary work, is an example of the need for further convincing examples and discussion of these matters. Thus, the present work includes new comprehensive fitting and model comparison results both for experimental data and for synthetic data generated from the latter.

In Section 2, some relevant common misconceptions are briefly summarized, and then in Section 3 a general time-to-frequency transformation is defined. Although it involves an arbitrary temporal correlation function, it nevertheless leads to a crucial distinction between the OMF and the CMF. The conventional choice of a definite form for the correlation function, a Kohlrausch stretched-exponential, leads in Section 4 to several distinct but related frequency-response models, the KD, K0, and K1 ones, and identifies the theoretical difference between OMF and CMF fitting models. Section 5 presents and discusses CMF and OMF fitting results for a representative experimental data set, as well as fits of synthetic data derived from it. Then Section 6 discusses and compares a dielectric-oriented fitting model alternative to the conductive-system CK1 one. In Section 7, crucial reasons are summarized why the OMF is incorrect and should be replaced by its corrected version, the CK1.

2. Some common misconceptions

There is an important distinction between just fitting data with any model at the electric modulus level and applying the OMF at this level. Unfortunately this distinction has not always been made clear [e.g., 2,8]. Thus, modulus-level fitting need not be assumed to be the same thing as OMF fitting, and the frequently used shortcut for identifying the OMF, the electric modulus, is a misnomer in this context.

Another potential stumbling block is the frequent characterization of the frequency response of materials dominated by mobile-charge conduction as dielectric relaxation ones [e.g., 2,7]. First, although "relaxation" is often taken as a general term, it is best restricted here to mean decaying response involving only a single relaxation time, i.e. separate Debye response or the characteristic relaxation time of a dispersive response model. In the usual case, the decay can be characterized as involving many such relaxation times, leading to dispersive behavior involving a distribution of individual relaxation times (DRT), usually taken to be continuous rather than discrete [3,6,9]. In such cases, Debye relaxation is the limit of dispersive response and involves a single discrete delta function DRT. The problem of discrimination between dielectric and conductive dispersive effects is discussed in Section 6.

In dielectric dispersion situations, the associated DRT involves dispersion of the dielectric-system physical processes, such as dipole rotation and vibration. In contrast, for dispersive conductive-system (CSD) situations, those the OMF was derived to represent, the associated DRT involves dispersion of the basic conduction process, such as ion hopping. Although the frequency response arising from such dispersion may be analyzed at the dielectric immittance level rather than at the complex resistivity

level, it is clearly inappropriate to characterize it as dielectric relaxation or dispersion, but instead to identify it as conductive-system dispersion, a more appropriate description than "conductivity relaxation" used, for example, in Refs. [1,7,8,10,11]. Here, I shall use the terms "dielectric constant" and "permittivity" interchangeably and usually take the "relative" modifier to be understood when appropriate. The bulk high-frequency-limiting relative permittivity of a material, not associated with charge hopping and diffusion, will be denoted here by $\varepsilon_{D\infty}$, a dimensionless dielectric quantity arising from induced and permanent dipoles and vibratory and electronic effects.

3. General transformations

Before defining the OMF and the CMF it is desirable to summarize the general transformations that lead to these models. We may start with the ordinary one-sided Fourier transformation of the time derivative of a temporal correlation function, $\phi_k(t)$:

$$I_k(\omega) = \int_0^\infty \exp(-i\omega t)\left(-\frac{d\phi_k(t)}{dt}\right)dt, \quad (1)$$

where $k = D$ or 0 [4,9,12]. The quantity $I_k(\omega)$ is a normalized frequency-response function that satisfies $I_k(0) = 1$ and $I_k(\infty) = 0$. When k is set equal to D in order to denote dielectric-system response [6,9,12], $-d\phi_D(t)/dt$ is the normalized transient decay current of a dielectric dispersion system after being fully charged. As usual, we shall use $\omega \equiv 2\pi\nu$ for theoretical quantities and ν for discussing data and fitting results.

The full dielectric-system frequency response may then be written as $\varepsilon_D(\omega) = \varepsilon_D(\infty) + \Delta\varepsilon_D I_D(\omega)$, where in general $\Delta\varepsilon \equiv \varepsilon_0 - \varepsilon_\infty$ and the high-frequency-limiting dielectric constant $\varepsilon_D(\infty)$ is denoted $\varepsilon_{D\infty}$ and taken frequency independent in the available experimental range. Dispersive response, involving the $I_D(\omega)$ function, may be modeled in terms of a DRT, and for the $k = D$ choice in Eq. (1) a distribution of dielectric relaxation times is involved [9,12].

Alternatively, when $k = 0$, one deals with conductive-system dispersive response, and the motion of mobile charges leads to a decay, at constant dielectric displacement, of the macroscopic electric field, E, represented by $E(t) = E(0)\phi_0(t)$ [1a,8,10]. Here, $\phi_0(t)$ is the mobile-charge correlation function, defined more explicitly below for a microscopic hopping model [13], and the $I_0(\omega)$ of Eq. (1) is then the corresponding normalized frequency response [4,6: p. 638]. Now define $\rho_0(\omega)$, the resistivity frequency-response function, and make the usual assumption that $\rho_0'(\infty)$ is zero or that it is so small that its effects are negligible in the available frequency range. Then we may write $\rho_0(\omega) = \rho_0'(0) I_0(\omega)$, and the associated electric modulus quantity is given by $M_0(\omega) = i\omega\varepsilon_V\rho_0(\omega)$, where ε_V is the permittivity of vacuum, and we shall just write $\rho_0 \equiv 1/\sigma_0 \equiv \rho'_0(0)$ hereafter.

Because $I_0(\omega)$ is defined at the resistivity immittance level for the $k = 0$ choice, rather than at the dielectric one for the $k = D$ choice, its DRT representation involves a distribution of resistivity, not dielectric, relaxation times [6]. In the OMF analysis [1a], its results, expressed at the complex M level, are characterized as "conductivity relaxation" rather than the more appropriate term "resistivity dispersion." Note that if the same functional form for $\phi_D(t)$ and $\phi_0(t)$ is used for the $k = D$ and $k = 0$ situations, the resulting $I_D(\omega)$ and $I_0(\omega)$ responses will be of exactly the same form but defined at the dielectric and resistivity levels, respectively [6].

Instead of setting $k = 1$ in Eq. (1), Moynihan and his co-authors [1] derived expressions for $k = 1M$ response by transforming $I_0(\omega)$ with the relation:

$$M_{C1}(\omega) = M'_{C1}(\omega) + iM''_{C1}(\omega) = i\omega\varepsilon_V\rho_0 I_1(\omega) \equiv [1 - I_{01}(\omega)]/\varepsilon_Z, \quad (2)$$

with ε_Z identified as $\varepsilon_{D\infty}$ and later written as just ε_∞, the full high-frequency limiting dielectric constant. These authors, and all subsequent users of the OMF, have written Eq. (2) with just the $I_{01}(\omega) = I_0(\omega)$ of Eq. (1) and have not employed the $I_0(\omega)$ function as the basis of a separate fitting model. Here, however, $I_0(\omega)$ is designated $I_{01}(\omega)$ in Eq. (2) to make the point that estimated values of the characteristic dispersion shape parameter and other parameters of the $I_0(\omega)$ response model must be obtained from fitting with the above $M_{C1}(\omega)$ model or with its resistivity level form $\rho_{C1}(\omega) \equiv \rho_0 I_1(\omega)$, not directly with the $k = 0$ model. The C subscript in Eq. (2) specifies conductive-system rather than dielectric-system dispersion (DSD), but for simplicity it will often be omitted hereafter.

Although general relations equivalent to the macroscopic OMF ones appeared ten years before it [14], of particular importance is the pioneering 1973 continuous-time-random-walk stochastic microscopic model of Scher and Lax [13], slightly extended later in Ref. [15]. Its general temporal correlation function, $\phi(t)$, equivalent to the $k = 0$ choice $\phi_0(t)$ function, is identified in Ref. [13] as the waiting time distribution for a hop, the probability that a mobile charge remains fixed in the time interval 0 to t.

The extended version of the Scher–Lax response model is fully isomorphic to that of Eq. (2) with the ε_Z quantity of Eq. (2) given by [4,6,15]

$$\varepsilon'_{C1}(\infty) \equiv \varepsilon_{C1\infty} = (\sigma_0/\varepsilon_V)\langle\tau\rangle_{01} = \varepsilon_{Ma}\langle x\rangle_{01} = [\gamma N(qd)^2/6(k_B\varepsilon_V)]/T, \quad (3)$$

with $x \equiv \tau/\tau_0$, and the Maxwell limiting dielectric constant quantity is $\varepsilon_{Ma} \equiv \sigma_0\tau_0/\varepsilon_V$. Here τ_0 is the characteristic relaxation time of the $I_0(\omega)$-model response function and $\langle\tau\rangle_{01}$ is the mean of τ over its DRT, with its shape parameter value determined from fitting with the Eq. (2) model; The quantity N is the maximum mobile charge number density; γ is the fraction of charge carriers of charge q that are mobile; d is the rms single-hop distance for a hopping entity, and k_B is the Boltzmann constant.

The high-frequency-limiting effective dielectric constant, $\varepsilon_{C1\infty}$, defined in Eq. (3), is obviously associated entirely with mobile-charge effects, and for ionic conduction it is likely to arise from the short-range vibrational and librational motion of caged ions. For the OMF situation, however, the result corresponding to that of Eq. (3) is [e.g., 1,2,8,10,11,16]

$$\varepsilon_Z = \varepsilon_\infty = (\sigma_0/\varepsilon_V)\langle\tau\rangle_0 = \varepsilon_{Ma}\langle x\rangle_0. \quad (4)$$

A principal and crucial difference between the OMF response model [1], including a great deal of later work using it of Ngai and co-authors and others, and the CMF model is the appearance in Eqs. (2) and (4) of $\varepsilon_Z = \varepsilon_\infty$ for the OMF and $\varepsilon_Z = \varepsilon_{C1\infty}$ in Eqs. (2) and (3) for the CMF. It is clear from Eq. (3), however, that the effective dielectric constant quantity $\varepsilon_{C1\infty}$ is a consequence only of conductive response, is zero in the absence of mobile charges, and does not include any bulk dipole dielectric effects, as, on the contrary, does the ε_∞ of the OMF [1b]. This trivially appearing difference, associated just with different definitions and interpretations of the ε_Z of Eq. (2), has far reaching consequences, as discussed in the next sections.

For completeness, it should be mentioned that Ngai and León [16] derived in 1999 a type of approximate isomorphism between the OMF and Scher–Lax models that required the introduction of two different time constants, a consequence of their conventional use of the OMF ε_∞ instead of $\varepsilon_{C1\infty}$. Its results were summarized in Ref. [8] of 2005 without reference to the 2002 work of the author [15] which led, as above, to full isomorphism without the need for two separate time constants.

4. Specific transformations and models

It will not have escaped the attention of the reader that no specific frequency-response models were fully defined in the last section. To do so, one must specify a form for $\phi_D(t)$ or $\phi_0(t)$. In the 1973 OMF treatment [1a], the authors followed the earlier dielectric-system $\phi_D(t)$ choice of Williams and Watts [12,17] and used in Eq. (1) the Kohlrausch stretched-exponential function:

$$\phi_k(t) = \exp[-(t/\tau_0)^{\beta_k}], \quad 0 < \beta_k \leqslant 1, \tag{5}$$

with $k = 0$ and β_k just written as β. Here β_k is the shape parameter and τ_0 is the characteristic relaxation time of the response function. Stretched-exponential behavior has been derived from many different theoretical assumptions, including the defect-diffusion random-walk model [18,19], and it has been experimentally observed for variety of materials such as polymers, ionic and molecular glasses, and super-cooled liquids.

For conductive-system situations, Eqs. (1) and (5) lead to a normalized $I_0(\omega)$ function whose full response, $\rho_0(\omega) = \rho_0 I_0(\omega)$, is called the K0 model when, as usual, ρ_∞ is negligible) [6,15]. Alternatively, for the $k = D$ dielectric situation, the use of a stretched-exponential $\phi_D(t)$ form leads to $\varepsilon_D(\omega) = \varepsilon_D(\infty) + \Delta\varepsilon_D I_D(\omega)$. The dispersed part of this response, the KD model, is just $\Delta\varepsilon_D I_D(\omega)$ [6,9,12].

Although the Kohlrausch $I_0(\omega)$ and $I_D(\omega)$ functions are the same in form, they apply at different immittance levels, as implied above, and they cannot be expressed in closed form except for values of their β_k shape parameters of 1/3, 1/2, 2/3, and 1. However, the free LEVM complex-nonlinear-least-squares (CNLS) computer program allows simulation and fitting of data using very accurate approximations for arbitrary values of β_k [20]. It is important to note that since both the $I_0(\infty)$ and $I_D(\infty)$ parts of the K0 and KD models are zero and thus lead to zero values of the high-frequency limiting dielectric constant, ε_∞, data fitting with these models should include the addition of a free capacitative parameter, C, in parallel with them. The resulting composite models will be denoted by CK0 and CKD, respectively.

Finally, once the $I_0(\omega)$ response function is available, one may use Eq. (2) to calculate $I_1(\omega)$ and its full resistivity-level model response, $\rho_1(\omega) = \rho_0 I_1(\omega)$, denoted the conductive-system OMF K1 model but not so named in Ref. [1a]. Alternatively, if the $I_0(\omega)$ DRT is known and/or is accurately calculable, as in LEVM, one can readily transform it to the DRT of $I_1(\omega)$ and then calculate $I_1(\omega)$ from it [6,12,21: see Eq. A.2].

The K1-model $I_1(\omega)$ normalized response function, when it is calculated from Eq. (2) with $I_0(\omega)$ derived from Eq. (1) using the stretched-exponential $\phi_0(t)$ of Eq. (5), is clearly only indirectly associated with stretched-exponential temporal response. The actual $\phi_1(t)$ response associated with the K1-model frequency response may be calculated either from its DRT or from its $I_1(\omega)$ response [4,12], and it approaches such a form only asymptotically in the limit of long times [22]. Further, as demonstrated in Ref. [23], the log–log slope of its normalized $\sigma'(\omega)$ response approaches its high-frequency limiting value appreciably slower than does equivalent K0-model response. Constraint theory shows that for charge motion in three dimensions for a macroscopically homogenous material with charges of a single-type mobile, the K1-model β_1 shape parameter should be exactly 1/3 [23]. When it is, the resulting quasi-universal model is denoted as the UN one [6,23].

It is worthwhile to explicitly distinguish between OMF and CMF models since they both involve the K1. Specifically, the OMF involves K1 response interpreted using the $\varepsilon_Z \equiv \varepsilon_\infty$ of Eq. (4) and uses the K1 model alone for fitting. In contrast, the CMF involves the K1 model interpreted using the $\varepsilon_Z \equiv \varepsilon_{C1\infty}$ definition of Eq. (3) and always requires for fitting a parallel capacitative parameter, denoted by C and representing $\varepsilon_{D\infty}$. Because of their importance, these distinctions are described in more detail in the next paragraph.

When the CMF K1 effective conductive-system dielectric constant $\varepsilon_{C1\infty}$ is not negligible, the full high-frequency-limiting dielectric constant is given by $\varepsilon_\infty = \varepsilon_{C1\infty} + \varepsilon_{D\infty}$. Since the CMF K1 model alone does not involve the endemic dielectric quantity $\varepsilon_{D\infty}$, when fitting with the K1 one must include a separate free parameter to represent the latter, and the resulting composite model is then denoted the CK1. No such free parameter is needed with OMF K1 fitting since the original assumption of this model is that the $\varepsilon_\infty = \varepsilon_{D\infty}$ of Eq. (4) "contains all the ordinary contributions to the relative permittivity of the material except those connected with the long-range ionic diffusion process" [1b]. Although the creators and subsequent users of the OMF do not recognize the existence of $\varepsilon_{C1\infty}$, OMF fitting with the K1 alone nevertheless leads to an estimate of ε_∞ and so may implicitly involve $\varepsilon_{C1\infty}$! The somewhat subtle differences between the OMF and the CMF response models mentioned above are at the heart of the incorrectness of the OMF model and its fitting results.

5. Representative CMF and OMF fitting results

In order to illustrate and justify some of the results and conclusions about the OMF and CMF data-fitting approaches described above, a frequency-response data set for the fast-ion material $0.35Li_2S \cdot 0.65GeS_2$ at 258 K, kindly supplied by Professor Steve Martin [24], has been analyzed in various ways and the results are presented in Tables 1–3 and in Figs. 1 and 2. It should be noted that the work of Ref. [24] makes use of the OMF but suggests some weaknesses of it. Since this data set showed appreciable electrode effects in the low-frequency region, a series constant-phase element was needed as part of a composite model to obtain good fits. Its form, expressed at the complex conductivity level, is $\sigma_{SC}(\omega) \equiv \varepsilon_V A_{SC}(i\omega)^{\gamma_{SC}}$, with A_{SC} frequency independent and γ_{SC} usually less than unity. Note that when $\gamma_{SC} = 1$, $\varepsilon_V A_{SC}$ is a specific capacitance. The $\sigma_{SC}(\omega)$ response function will be denoted here by S, so a composite fitting model including the CK1 and a series constant-phase element is denoted by CK1S [25–27]. Similarly, the dielectric-system CKD model becomes CKDS [28].

One important test of the adequacy of a fitting model is to compare the values and uncertainties of the estimated values of the free parameters of the model for full CNLS fits with the data expressed at different immittance levels. In the absence of systematic and random errors the results should be independent of the fitting level. Much of the present work involves fitting with proportional weighting (PWT) which treats large and small data values equally [20]. Independent of the presence of systematic and random errors the use of such weighting leads to identical parameter estimates for M and ρ level fits and, separately, for σ and ε ones, so only fits at two of the four immittance levels are necessary for such comparisons. Table 1 presents the results of comparisons for the CK1S, CUNS, and RCKDS models. The R symbol of the RCKDS composite model denotes the presence of a frequency-independent ρ_0 resistivity in parallel with the rest of the model.

In the present tables, $100S_F$ is the percent relative standard deviation (RSD) of the residuals of a fit; when it is less than 3% the fit is good, and it is very poor for values of 10% or more. The quantity PDRMS is the root mean square of the relative standard deviations of the parameters, with the RSD of the τ_0 parameter generally the largest of these values. For good fits both S_F and PDRMS values should be small. The subscript k of β_k may be D, 0, 1, or 1M (for OMF fits such as those using the K1 and K1S models).

Table 1
LEVM CNLS fits of $0.35Li_2S \cdot 0.65GeS_2$ 76-point frequency response data at 258 K with various CK1S, CUNS, and RCKDS composite models, all with proportional weighting (PWT).

Fit model levels	$100S_F$ PDRMS	$10^{-6}\rho_0$ RSD	$10^{7}\tau_0$ RSD	β_k RSD	$\varepsilon_{C1\infty}$ or $\Delta\varepsilon$ RSD	$\varepsilon_{D\infty}$ RSD	ε_∞ RSD	$10^{-6}A_{SC}$ RSD	γ_{SC} RSD
CK1S	2.14	1.04	2.12	0.337	13.26	28.84	42.10	1.73	0.839
M,ρ	0.078	0.0026	0.185	0.025		0.039		0.0065	0.0022
C_FK1S	2.13	1.04	2.12	0.337	13.26	28.84F	42.10	1.73	0.839
M,ρ	0.011	0.0025	0.024	0.0039				0.0065	0.0021
CK1S*	2.14	1.04	2.12F	0.344	14.35	27.82	42.17	1.73	0.839
M,ρ	0.0041	0.0025		0.0012		0.0053		0.0065	0.0021
CUNS	2.13	1.04	1.97	1/3F	12.78	29.28	42.06	1.73	0.839
M,ρ	0.0056	0.0025	0.0083			0.0053		0.0065	0.0021
RCKDS	1.58	1.05	192	0.430	124.6	–	42.59	1.72	0.842
M,ρ	0.022	0.0019	0.057	0.0087	0.015		0.0031	0.0048	0.0016
CK1S	2.07	1.05	2.49	0.344	14.30	27.88	42.17	1.71	0.841
σ,ε	0.068	0.0024	0.160	0.022		0.041		0.0042	0.0017
C_FK1S	2.06	1.05	2.49	0.344	14.30	27.88F	42.17	1.71	0.841
σ,ε	0.019	0.0024	0.041	0.0065				0.0042	0.0016
CK1S*	2.06	1.05	2.49F	0.344	14.30	27.88	42.17	1.71	0.841
σ,ε	0.0053	0.0024		0.0012		0.011		0.0042	0.0016
CUNS	2.08	1.05	1.97	1/3F	12.74	29.37	42.11	1.71	0.842
σ,ε	0.0066	0.0025	0.0085			0.011		0.0042	0.0016
RCKDS	1.43	1.05	182	0.430	123.0	–	42.65	1.71	0.844
σ,ε	0.018	0.0017	0.046	0.0073	0.012		0.0047	0.0029	0.0012

In the CK1S model, the letter C represents the free $\varepsilon_{D\infty}$ parameter, but this parameter is fixed at its free-fit value for the C_F K1S fits, and those designated CK1S* involve values of τ_0 fixed at their free-fit values. Here RSD denotes the relative standard deviation of a free-fitting parameter, and the letter F, as in 1/3F, indicates that the value is fixed during fitting. The subscript k in β_k is either 1 or D here, depending on the model type.

Table 2
LEVM CNLS and NLS fits of $0.35Li_2S \cdot 0.65GeS_2$ 76-point frequency response data at 258 K with various Kohlrausch-derived composite models.

Row number	Fit model	Level	Weight	$100S_F$ PDRMS	RSD of τ_0	β_k or β_{1M}	$\varepsilon_{C1\infty}$	$\varepsilon_{D\infty}$	ε_∞
1	CK0S	M	PWT	2.74 0.0066	1.1×10^{-2}	0.537	–	–	43.62
2	CK1S	M	PWT	2.14 0.078	0.185	0.337	13.26	28.84	42.10
3	K1S	M	PWT	3.01 0.0069	1.1×10^{-2}	0.473	–	–	43.85
4	K1S	M	UWT	96 0.293	6.8×10^{-3}	0.501	–	–	46.88
5	K1S	σ'	PWT	1.34 0.165	0.365	0.357	16.50	–	–
6	K1S	σ'	UWT	3.74 0.182	0.399	0.325	12.52	–	–
7	CUNS/K1S	M	PWT	1.50 0.0034	5.3×10^{-3}	0.473	–	–	43.85
8	K1S3/CUNS	M	PWT	1.50 0.0039	5.7×10^{-3}	1/3F	12.80	29.30	42.10

For row-7, an exact data set calculated from the CUNS fit parameters of Table 1 was fitted by the OMF K1S model, and for row-8 a row-3 exact K1S data set was fitted by the CUNS model.

The RSD estimates for the two Table 1 CK1S τ_0 fit results are particularly large, arising from a very high correlation between the τ_0 and β_1 parameters. To further investigate this behavior, for each separate level fitting, two more CK1S fits, in which one model parameter is fixed at its originally estimated value, as well as a CUNS fit, where β_1 is fixed at 1/3, are included. The principal effect for all three of these fixed-parameter fits is a great reduction in the RSD values of the remaining CK1-model free parameters, without much change in their estimated values, thus providing more confidence in these values. The CK1S β_1 estimates of 0.337 and 0.344 are so close to 1/3 that the CUNS-model fit is the most appropriate model for representing the present data at any immittance level.

Although the $100S_F$ values in Table 1 indicate that the present fits are good but not exceptionally good, comparison of parameter values and RSDs for the M, ρ and those for the σ, ε level fits nevertheless shows that they are quite stable and adequately consistent. Thus fits for either level may be used for data interpretation. The RCKDS results are discussed in Section 6.

Table 2 presents fit results for conductive-system composite models involving Kohlrausch-derived parts. The CK0S-model fit results are comparable to those of the CK1S and CUNS models in Table 1 but lead to a much larger β_0 estimate and to no separate $\varepsilon_{C1\infty}$ and $\varepsilon_{D\infty}$ estimates. Even though the OMF K1S model has the same number of free parameters as the CMF CUNS one and one less than the CK1S model, the $100S_F$ value of the latter is somewhat smaller than that of the comparable row-3 OMF fit result. Further, the β_{1M} OMF estimates of rows 3 and 4 are much larger.

Finally, the OMF K1S fits of rows 3–6 show the expected large difference between the β_{1M} M-level fit estimates and the σ' ones. As expected, the σ' values are close to 1/3. Further, although all

Table 3
LEVM CNLS and NLS OMF K1-model fits of exact CUN-model 121-point, 0.1–10^{11} Hz, frequency response data calculated from the CUNS-model fit parameters of Table 1, row 4.

Row number	Fit model	Level	Weight	$100S_F$	RSD of τ_0	β_1 or β_{1M}	$\varepsilon_{C1\infty}$	ε_∞
1	CUN	M	PWT	Exact	Exact	1/3F	12.78	42.06
2	K1	M	PWT	10.92	1.5×10^{-2}	0.425	–	41.42
3	K1	M	UWT	20.70	7.2×10^{-3}	0.449	–	42.66
4	K1	M'	PWT	1.55	9.5×10^{-3}	0.462	–	42.73
5	K1	M'	UWT	21.73	9.3×10^{-3}	0.446	–	44.55
6	K1	M''	PWT	10.80	1.7×10^{-2}	0.398	–	45.62
7	K1	M''	UWT	25.86	1.2×10^{-2}	0.460	–	43.03
8	K1	σ	PWT	12.44	3.5×10^{-2}	0.420	–	37.11
9	K1	σ	UWT	70.43	3.4×10^{-4}	0.338	–	42.06
10	K1	σ'	PWT	3.98×10^{-8}	8.2×10^{-8}	1/3	12.78	–
11	K1	σ'	UWT	3.59×10^{-6}	1.9×10^{-5}	1/3	12.78	–
12	K1	σ''	PWT	1.23	1.6×10^{-2}	0.462	–	42.98
13	K1	σ''	UWT	65.56	3.0×10^{-3}	0.352	–	42.08
14	K1	ρ	UWT	17.88	1.1×10^{-2}	0.467	–	41.71
15	K1	ρ'	UWT	25.30	1.5×10^{-2}	0.467	–	41.89
16	K1	ρ''	UWT	5.09	1.8×10^{-2}	0.466	–	41.08
17	K1	ε	UWT	16.59	8.8×10^{-3}	0.459	–	42.08
18	K1	ε'	UWT	1.37	1.4×10^{-2}	0.463	–	43.27
19	K1	ε''	UWT	7.17×10^{-8}	1.5×10^{-7}	1/3	12.78	–

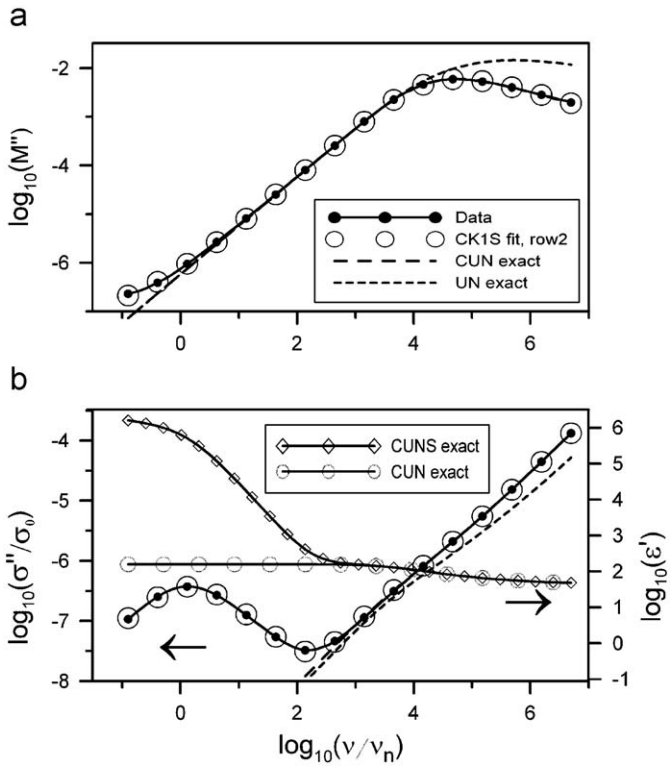

Fig. 1. CNLS fits of $0.35Li_2S\cdot0.65GeS_2$ frequency-response data at 258 K. (a) M'' results of CK1S-model fit, rows 1 or 2 of Table 1, at the M level with proportional weighting (PWT); exact CUN response (no series elements) and exact UN-model response (no parallel bulk dielectric parameter, $\varepsilon_{D\infty}$). (b) Same results as in (a) but at σ'' level; comparison at the ε' level of exact CUNS response and that of CUN. The normalization quantity ν_n is 1 Hz and σ_0 is 1 S/cm.

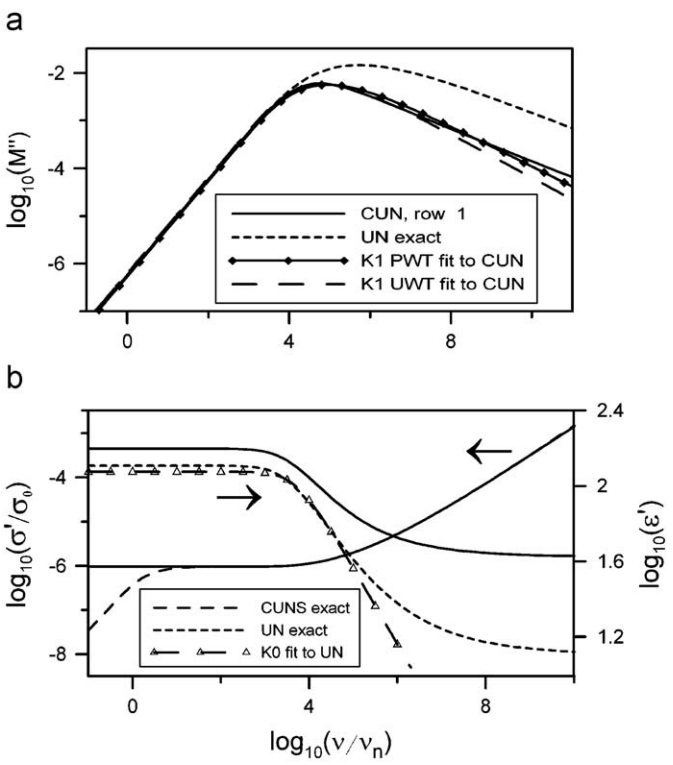

Fig. 2. Exact extrapolated data and responses calculated from the parameters of the CUNS fit of row-4, Table 1. (a) Comparison of CUN and UN M''-level responses and also those of OMF K1-model fits to the CUN data using unity weighting (UWT). (b) Comparison of CUNS and CUN σ'-level responses (the same here as UNS and UN ones); ε'-level comparison of CUN and UN responses, and that of a K0-model PWT fit to exact UN data.

the ε estimates of these fits are actually calculated using fit parameter estimates in Eq. (3) and so are what CMF users would call $\varepsilon_{C1\infty}$ and OMF ones would call ε_∞, their values have been placed in appropriate columns in the table. Incidentally, for the present temperature a β_{1M} estimate cited in Ref. [24b] and called β_σ was 0.48, in good agreement with the estimates in rows 3 and 4. The inconsistency between M-level and σ'-level β_{1M} estimates for either PWT or unity weighting (UWT), the crux of the failure of the OMF approach, is further demonstrated by results presented in Table 3.

It is of interest to compare how well exact CMF synthetic data calculated from Table 1 CUNS-model fit parameter estimates is fitted by the OMF K1S model, and *vice versa*. Results are presented in rows 7 and 8 of Table 2. Comparison of row-7 results with row-3 ones and of row-8 results with the CUNS ones of Table 1 shows close agreement between the corresponding parameter estimates.

In Table 3 we follow the same procedure, using a wider frequency range and omitting the constant-phase element part of the response in order to generate exact data and bare-bones OMF fitting results for all immittance levels.

The solid data lines in Fig. 1 were plotted using all the data points, but to avoid congestion only every fifth point is shown as a small solid circle. CK1S-model fit points are depicted by open circles. The accuracy of the fits is demonstrated by the degree to which the open circles encircle the data points uniformly [28]. Here, only the lowest-frequency M'' point shows a small deviation. Note that although Fig. 1a results show that electrode effects play only a small role at low frequencies for the M'' results, the σ'' results of 1b show dominant low-frequency electrode effects, very well fitted by the series constant-phase element S-part of the CK1S model. Although such effects play too small a role at high frequencies to be resolved on the present log–log plot, they are often found to be important in this region [25–27].

Below about 1 KHz the CUNS ε' response curve of Fig. 1b shows an increase of several orders of magnitude as the frequency decreases. Comparison between the CUNS and the CUN responses demonstrates that this growth is entirely due to the series constant-phase element, S; thus it is unrelated to the dispersive UN bulk response and is therefore most likely associated with processes at the electrodes, possibly with fractal behavior [29] and specific adsorption [30]. The much smaller dispersive CUN and UN responses are presented on an expanded scale in Fig. 2b. In addition, the results of a CNLS K0-model proportional-weighting fit to the exact UN data demonstrate in this figure that $\varepsilon_{C0\infty}$ is zero for this model. For this fit the β_0 estimate was about 0.59.

Because OMF data fits usually involve only M or M'' immittance-level data and often use the results listed in Table 2 of Ref. [1a] to estimate approximate β_{1M} values from the width of a $M''(\omega)$ curve at half-height, it is worthwhile to compare accurate OMF K1-model fit results for all 12 immittance levels using both PWT and UWT. Since the CUNS-model fit results in the fourth row of Table 1 represents the data very well, we may use its parameter estimates in LEVM to generate exact CUN extended-range response data, as shown in row 1 of Table 3. It thus well represents the original experimental data with all electrode effects removed.

Table 3 shows the results of PWT and UWT K1-model fits to the row-1 CUN data set. Only 18 rather than 24 fits are required because, as already mentioned, with PWT the results for data expressed at the $\rho(\omega)$ and $M(\omega)$ levels are exactly the same, as are those expressed at the $\sigma(\omega)$ and $\varepsilon(\omega)$ levels. The results in Table 3 show variation in β_{1M} estimated values over a range from about 0.40 to 0.47, omitting the values of rows 9, 10, 11, 13, and 19. The 1/3 fit estimates of rows 10, 11, and 19 each involved six or seven correct decimal-place values, as expected from the row-1 exact value. The β_{1M} values of rows 9 and 13 were surprisingly close to 1/3. It is clear that the fits leading to the correct $\beta_{1M} = \beta_1$ values of 1/3 are entirely inconsistent with all the others.

Comparison of β_{1M} estimates for comparable K1S fits of Table 2 with the K1 ones of Table 3 indicates that the presence of electrode effects and a restricted frequency range for Table 2 data lead to somewhat larger values of β_{1M} than those for the exact CUN data of Table 3. Of course, fitting with CMF models obviates these OMF model discrepancies.

Fig. 2b shows the effect on $\sigma'(\nu)$ at low frequencies of the series electrode function included in CUNS response compared to that of CUN. In addition, it demonstrates that the K0 model involves no non-zero $\varepsilon'(\infty)$, and that the capacitance parts of the UN and CUN models lead to the high-frequency limiting values of $\varepsilon_{C1\infty}$ and $\varepsilon_\infty = \varepsilon_{C1\infty} + \varepsilon_{D\infty}$ respectively.

Fig. 2a illustrates the large high-frequency differences between the UN and CUN $M''(\nu)$ responses. In addition, this figure includes response curves for Table 3 rows 6 and 7 K1 $M''(\nu)$ PWT and UWT fits to the CUN data. Note that both the PWT and UWT K1 OMF curves fall below the exact CUN response curve at high frequencies. In the past, such response, particularly that involving UWT or its equivalent, always found with OMF fitting of experimental data for ionic glasses at sufficiently high frequencies [1a,8], has been characterized as "excess wing" behavior, but since the OMF is an invalid fitting model, such usage is misleading and should be rejected because no excess wing appears with CK1 rather than with K1 fitting. It is this failure of the OMF model to fit extended high-frequency data that leads here to the very poor $100S_F$ values of most of the K1 fits listed in Table 3. But even for the restricted-range data of Table 2 the use of the OMF K1S model leads to erroneous M-level β_{1M} values, another indication of its inappropriateness.

6. Comparison of and discrimination between conductive-system and dielectric-system fitting models

A perennial problem with immittance spectroscopy analysis of data from condensed-matter materials has been the need to decide whether the data involve dispersed CSD response associated with ionic motion or whether such response involves DSD dipolar effects. Even when the material of interest exhibits appreciable ionic conductivity, its response has sometimes been characterized as dielectric and any dispersion present ascribed to dipoles rather than to ions. Therefore the history and present status of the matter needs attention.

In the absence of dispersion, any material of interest will involve a dc conductivity σ_0, and a high-frequency-limiting bulk permittivity $\varepsilon_{D\infty}$, leading to simple Debye relaxation response, of conductive-system character when these elements are in parallel and to dielectric-system behavior when they are in series.

In non-dispersive dielectric materials without impurity ions, σ_0 will be very small and may fall below the lower measurement limit. Usually, however, the presence of some thermally activated impurity ions can lead to values within the available measurement range by picking a high enough material temperature. Then estimates of both σ_0 and $\varepsilon_{D\infty}$ may be obtained by fitting the frequency response of the system with an appropriate Debye model: a simple instance of immittance spectroscopy.

The situation is different when dispersion is present [28,31,32]. Consider first that where only CSD is present. Then σ_0 is the low-frequency-limiting conductivity value of the dispersive model when, as in the usual case, the high-frequency resistivity limit is zero or negligible. In this case a peak in the M'' response will always be possible, even in the absence of any parallel capacitance.

Alternatively, for DSD the low-frequency-limiting value of the dispersion function alone is $\Delta\varepsilon$, and a parallel capacitance, represented by $\varepsilon_{D\infty}$ is required for a peak in M'' response to appear. One cannot distinguish between the two dispersion types of dispersion from immittance measurements alone because Maxwell's equations ensure that both conductive and displacement contributions to the total current appear together. Finally, both conductive and dielectric dispersion effects may be simultaneously present in the data [28]. Even in this case, one would like to establish whether the main dispersion is conductive or dielectric in character.

Results of data fitting of exact synthetic data, published in 1999 [33], illustrate the problem of discrimination between dispersive conductive and dielectric responses. It involved fitting data calculated using a CSD CK1 model with a DSD one and the

inverse problem of fitting exact DSD data with a CSD model. Excellent fits were found in both cases, precluding the possibility of an absolute choice.

Since 1973, it has usually been assumed that materials with appreciable mobile-ion concentrations are of conductive-system character and thus involve a distribution of resistivity relaxation times [e.g., 1,6,8,15,23,26]. The OMF and CK1 models have been widely used for the analysis of such materials, but even the CK1 is inappropriate when the dispersion is actually of dielectric character.

The latter assumption has been made in the work of Johari and co-authors [e.g., 31,32] who fitted glasses, polymers, and ionic melts with a model involving a frequency-independent σ_0 (associated with long-range ionic motion) in parallel with a dispersive dielectric-level dipolar model, such as that of Davidson and Cole [12]. They established that the DSD approach was superior to the CSD OMF one, but they did not use CNLS fitting or the CK1 model since the latter model was not then available. Since their work, there has been little detailed attention to the discrimination problem until recently [28,33], and a choice based on ionic dominance or molecular character has usually been made without any data-fitting comparisons of dispersion possibilities.

It should be noted that although ion hopping is assumed to lead to CSD response in materials with appreciable ionic conductivity, in such circumstances the alternate Johari DSD approach also involves dipoles, usually identified as arising from ion pairs. It seems, however, that dispersed ion hopping, which involves a DRT with very many different times between hops, is likely to be more physically plausible than a DRT assumed to arise from less-mobile-ion pairs.

Besides the generally excellent CK1 and CUN fits of data for many ionic solids listed in Refs. [23,26,30], it was recently shown in Ref. [34] that the CK1S model, plus additional CSD series elements, well fitted fused-salt CKN data for several temperatures up to frequencies of 10^{11} Hz and even predicted the observed Boson peak present at about 3×10^{12} Hz. In contrast, the work of Ref. [28] dealt with the discrimination problem by analysis of the responses of the super-cooled liquids NMEC and glycerol above their glass transition temperatures. Both these non-associated viscous liquids exhibited appreciable ionic impurity conduction.

Therefore, their data sets for several temperatures were fitted with both CSD and DSD composite-model approaches, as well as combinations thereof. The best CSD model involved a series combination of the CK1 and Debye models, with the latter accounting for a very high resistivity ρ_0 probably associated with partial blocking of ions at the electrodes. A composite DSD, CSD model was found more appropriate, however, and involved a parallel combination of R, C, and a dielectric-level Davidson–Cole model (DCD), all in series with a resistivity-level CSD Davidson–-Cole model (DC0). Here the R element again represented ρ_0, and the DCD model response dominated that of the DC0 one. Therefore, for these data sets both fitting results and physico-chemical evidence made it highly likely that the main α-dispersion was of dipolar character but did not strongly discriminate between ion-pair dipoles and permanent and induced molecular ones.

One approach that might help in unraveling the mystery of the cause of observed dispersive behavior is to experimentally vary the concentration of ions (mobile and immobile) at constant measurement temperature when this is possible. For a sufficiently small ionic concentration approaching zero, there will be no conductive-system dispersion observable and any dispersion still present must arise from a dipole DRT. Results shown in Table 2 of Ref. [26] indicate that a reduction by a factor of 30 of the ion concentration, x, in $x\mathrm{Na_2O}(1-x)\mathrm{GeO_2}$ fitted by a CSD model led to a substantial reduction in ε_∞ toward $\varepsilon_{D\infty}$ but to very little change in $\varepsilon_{D\infty}$, as might be expected in the absence of ion-pair dispersion.

Finally, it is worthwhile to consider discrimination possibilities for the fast-ion $0.35\mathrm{Li_2}\cdot0.65\mathrm{GeS_2}$ fitting results summarized in Table 1. Since results for M, ρ fitting are comparable to those for σ, ε, I shall consider only the M, ρ ones. First, fits with a DSD RCDCDS Davidson-Cole model led to $100S_F$ and PDRMS values of 2.37 and 0.026, respectively, appreciably larger than those of the RCKDS fit in row 5 of Table 1. Secondly, it was not found possible to obtain a viable fit for this data set that included both DSD and CSD dispersion models in a composite model, although that was possible for the molecular-liquid fits considered in Ref. [28].

Although the composite-model RCKDS fit of row 5 led to a slightly smaller $100S_F$ value than that of the CUNS in row 4, it involves two more free parameters than does the CUNS. More important is that the PDRMS of the RCKDS fit is far larger than the CUNS one because two of the RCKDS parameter uncertainties are large. Although these results are not definitive, they suggest that a CSD model fit is more appropriate here than a DSD one. But the large estimated value of $\varepsilon_{D\infty}$, over 42 here, nevertheless suggests that it primarily arises from probably non-dispersed, ion-pair effective dipoles.

Virgil said, *Felix qui potuit rerum cognoscere causus* (“Happy is the one who can know the causes of things”). For the presently discussed discrimination tasks, it seems that, thanks to Maxwell, we are fated to remain unhappy!

7. Crucial inconsistencies of the original modulus formalism

From a theoretical point of view one might think that pointing out that using purely conductive-system model parameters to represent both conductive and dielectric effects, as in the OMF, should be sufficient to invalidate such a model. One might also think it reasonable that such a model should be invalidated by the experimental demonstration of the irreconcilable inconsistency between β_{1M} estimates obtained from $M(\omega)$ and/or $M''(\omega)$ OMF K1-model data fitting and those found from such $\sigma'(\omega)$ and/or $\varepsilon''(\omega)$ fittings. These expectations, reasonable as they may seem, continue however to be entirely ignored by the proponents and users of the OMF. A possible motivation for ignoring and not responding to criticism is simple: Do not respond if the criticism cannot be refuted because to do so would require an admission that both the theory and its physically based conclusions are erroneous, thus accepting that much prior work is invalid.

It is therefore worthwhile to describe in more detail the several crucial inconsistencies of the OMF approach, one of them not explicitly mentioned previously. Since both the OMF and CMF use the same K1 model, their only difference at the K1 level is their interpretations of the ε_Z of Eq. (2). While there is no essential difference in the calculations of the $\varepsilon_{C1\infty}$ of Eq. (3) and of the ε_∞ of Eq. (4), since both involve fitting estimates of the purely conductive-system quantities σ_0 and τ_0, an $\varepsilon_{C1\infty}$ estimate involves such values following from a CMF CK1 or CUN fit, while the ε_∞ of Eq. (4) follows from a K1 OMF fit, usually leading to quite different and unacceptable OMF results, as demonstrated in the foregoing sections.

One might argue that since OMF fits lead to reasonably good estimates of ε_∞, the OMF is a valid approach. But they also lead to inconsistent estimates of β_{1M}, to an excess wing, and to physically improper τ_0 estimates, as discussed below. Although the presence of an excess wing is recognized but not explained in Ref. [8], its importance is downplayed there. The increase of β_{1M} with

increasing temperature and with decreasing concentration of mobile ions has been cited by Ngai as evidence for ion-ion correlation, and β_{1M} estimates have been routinely used in his coupling model [7,10,22,35]. Both this conclusion and its application must, however, be rejected because of the crucial inconsistency of the OMF. The alternate use, in both the coupling model and in a superior DRT cutoff model, of the CMF β_1, whose value is virtually independent of variations in the above exogenous variables, is discussed in Ref. [35].

Finally, consider what happens as the relative concentration of mobile ions in a given material decreases towards zero. There is no problem with the CMF approach. As shown by Eq. (3), $\varepsilon_{C1\infty}$ goes to zero, and therefore ε_∞ properly approaches $\varepsilon_{D\infty}$, the C quantity in the CK1 model [6,23,26]. These results are just as one would expect: in the absence of mobile ions the capacitative effect of the ions disappears and all that is left is the bulk dipolar dielectric constant $\varepsilon_{D\infty}$. As shown in Fig. 7 of Ref. [6], as the concentration decreases and the $\varepsilon_{C1\infty}/\varepsilon_{D\infty}$ ratio approaches zero, the dispersive K1 part of the CK1 model appears at higher and higher frequencies relative to the dominant Debye response involving the relaxation time $\rho_0\varepsilon_V\varepsilon_{D\infty}$, response which itself disappears at zero mobile-ion concentration.

The situation is different for the OMF, one where the ε_∞ of Eq. (4) was defined in 1972 as $\varepsilon_{D\infty}$ [1b], and no such quantity as $\varepsilon_{C1\infty}$ is ever defined or recognized. But Eq. (4) nevertheless involves only mobile-ion quantities and so, taken literally, leads to ε_∞ reaching zero in the absence of mobile charges, not to $\varepsilon_{D\infty}$. Of course, this is contrary to the results of all experimental measurements and is not what actually happens, even with the OMF K1 model.

Instead, fits of experimental modulus data with the K1 alone also lead to ε_∞ estimates approaching $\varepsilon_{D\infty}$ as the ionic concentration approaches zero. The OMF calculation of ε_∞ involves the ionic-related quantities ρ_0 and τ_0 and, in the absence of any parallel parameter representing $\varepsilon_{D\infty}$ as in the CMF, K1-model fitting of data that intrinsically involves $\varepsilon_{D\infty}$, leads to estimates of ρ_0 and τ_0 that try to account for its presence. Since most models lead to good estimates of ρ_0 when any electrode effects are adequately accounted for, it is primarily the τ_0 variable that must adjust to allow a good fit. The Table 2 τ_0 estimates for the CK0S (M), CUNS (M), K1S (M), and K1S (σ') fits are 5.44×10^{-6}, 1.97×10^{-7}, 1.82×10^{-6}, and 3.27×10^{-7} s, respectively. One would expect the CUNS and K1S (σ') values to be close since they are both CMF fits, and although the τ_0 estimate for the latter fit was poor, it agrees within about one of its standard deviations with the CUNS one.

For comparison with the above τ_0 estimates, the τ_{0p} values corresponding to the frequency of the M'' peak of the present data and to that of its UN fit are 2.83×10^{-6} and 2.94×10^{-7} s, respectively. The presentτ_0-fit results make it quite clear that, just as OMF M-level β_{1M} estimates are incorrect, corresponding τ_0 ones are wrong as well.

Acknowledgment

Many thanks are due to Dr. Kia L. Ngai, whose creative and extensive papers using the original modulus formalism, the Ngai coupling model, and rejection of the possibility of exact Debye relaxation have stimulated me to keep busy in retirement.

References

[1] (a) C.T. Moynihan, L.P. Boesch, N.L. Laberge, Phys. Chem. Glasses 14 (1973) 122 See also;
(b) P.B. Macedo, C.T. Moynihan, R. Bose, Phys. Chem. Glasses 13 (1972) 171.
[2] K.L. Ngai, R.W. Rendell, Phys. Rev. B 61 (2000) 9393.
[3] B.A. Boukamp, J.R. Macdonald, Solid State Ionics 74 (1994) 85 See especially Appendix 1.
[4] J.R. Macdonald, J. Non-Cryst. Solids 197 (1996) 83 Erratum: 204 (1996) 309. In addition, in Eq. (A2) G_D should be G_{CD}.
[5] J.R. Macdonald, J. Appl. Phys. 95 (2004) 1849.
[6] J.R. Macdonald, J. Phys.: Condens. Matter 18 (2006) 629 On p. 640, next to bottom line, replace $\rho_0\varepsilon_{D\infty}$ by $\rho_0\varepsilon_V\varepsilon_{D\infty}$. The word "imaginary" on the third line of p. 643 should be replaced by "real.".
[7] K.L. Ngai, J. Habasaki, Y. Hiwatari, C. León, J. Phys.: Condens. Matter 15 (2003) S1607.
[8] I.M. Hodge, K.L. Ngai, C.T. Mohnihan, J. Non-Cryst. Solids 351 (2005) 104 In a private communication Dr. Hodge has informed me that he was unaware, while writing this paper, of my publications criticizing the OMF and was not informed of them by his co-authors.
[9] J.R. Macdonald, J. Chem. Phys. 102 (1995) 6241.
[10] K.L. Ngai, Philos. Mag. B 77 (1998) 187.
[11] K.L. Ngai, C. León, J. Non-Cryst. Solids 315 (2003) 124.
[12] G.P. Lindsay, G.D. Patterson, J. Chem. Phys. 73 (1980) 3348.
[13] H. Scher, M. Lax, Phys. Rev. B 7 (1973) 4491.
[14] J.R. Macdonald, C.A. Barlow Jr., Rev. Mod. Phys. 35 (1963) 940.
[15] J.R. Macdonald, Solid State Ionics 150 (2002) 263.
[16] K.L. Ngai, C. León, Phys. Rev. B 60 (1999) 9396.
[17] G. Williams, D.C. Watts, Trans. Faraday Soc. 66 (1970) 80; Trans. Faraday Soc. 67 (1971) 1323.
[18] M.F. Shlesinger, E.W. Montroll, Proc. Natl. Acad. Sci. USA 81 (1984) 1280.
[19] J.T. Bendler, J.J. Fontanella, J. Chem. Phys. 118 (2003) 6713.
[20] J.R. Macdonald, L.D. Potter Jr., Solid State Ionics 23 (1987) 61; J.R. Macdonald, J. Comput. Phys. 157 (2000) 280 The newest WINDOWS version, LEVMW, of the comprehensive LEVM fitting and inversion program may be downloaded at no cost by accessing 〈http://jrossmacdonald.com〉. It includes an extensive manual and executable and full source code. More information about LEVM is provided at this internet address. Nearly all the papers of the author cited herein are available for downloading in PDF format from the above webpage address.
[21] J.R. Macdonald, J. Non-Cryst. Solids 212 (1997) 95 The symbol σ should be removed from the right end of Eq. (12).
[22] J.R. Macdonald, J. Appl. Phys. 84 (1998) 812.
[23] J.R. Macdonald, Phys. Rev. B 71 (2005) 184307.
[24] (a) K.H. Kim, D.R. Torgeson, F. Borsa, J. Chu, S.W. Martin, I. Svare, Solid State Ionics 91 (1996) 7;
(b) I. Svare, S.W. Martin, F. Borsa, Phys. Rev. B 61 (2000) 228.
[25] J.R. Macdonald, J. Non-Cryst. Solids 307–310 (2002) 913.
[26] J.R. Macdonald, J. Chem. Phys. 116 (2002) 3401.
[27] J.R. Macdonald, J. Phys.: Condens. Matter 17 (2005) 4369.
[28] J.R. Macdonald, J. Phys. Chem. 112 (2008) 13684.
[29] G.A. Niklasson, J. Phys.: Condens. Matter 5 (1993) 4233.
[30] J.R. Macdonald, M.M. Ahmad, J. Phys.: Condens. Matter 19 (2005) 046215.
[31] G.P. Johari, K. Pathmanathan, Phys. Chem. Glasses 29 (1988) 219.
[32] M.G. Parthun, G.P. Johari, J. Chem. Soc. Faraday Trans. 91 (1995) 329.
[33] J.R. Macdonald, Braz. J. Phys. 29 (1999) 332.
[34] J.R. Macdonald, J. Phys. Chem. 111 (2007) 7064.
[35] J.R. Macdonald, Solid State Ionics 176 (2005) 1961.