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# Comment: Re-evaluation of a Coulomb-fluctuation frequency-response model for disordered conductors

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**Abstract**

Various problems and limitations of a recent Coulomb-fluctuation model by Bondarev and Pikhitsa [Phys. Lett. A 196 (1994) 247] for the transient and frequency response of disordered conductors are considered. The model can be expressed in terms of a simple Gaussian distribution of activation energies, contains an inconsistency, and is of much less general applicability than is claimed by its authors.

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## 1. Introduction

Recently, Bondarev and Pikhitsa [1] (abbreviated hereafter as BP) have published an interesting treatment of the transient and frequency responses of a disordered conductor associated with Coulomb fluctuations of the field of mobile charged defects, such as ions. Their response equations, expressed only in quadrature form, were used to obtain numerical values for comparison with the measured frequency response of superionic Na $\beta$-alumina and with exact Kohlrausch–Williams–Watts (KWW) stretched-exponential transient response in dimensionless form [2],

$$f_K(t) = f_K(0)\exp\left[-(t/\tau_K)^{\beta}\right], \qquad (1)$$

using $f_K(0) = 1$. The good agreement they showed between the predictions of their theory and these frequency and transient responses seems to support their claims that their approach yields "universal frequency response" and "allows one to give a complete quantitative description of a large number of experimental data on the relaxation dynamics of disordered conductors". But, as discussed below, these claims are unjustified.

Define $\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega)$ as the complex conductivity and $\sigma(0) \equiv \sigma'(0)$ as the DC conductivity. The corresponding complex resistivity is $\rho(\omega) = \sigma(\omega)^{-1} = \rho'(\omega) + i\rho''(\omega)$, and $\rho(0) = \sigma(0)^{-1}$. By universal frequency response, BP mean that $\Delta\sigma(\omega) \equiv \sigma'(\omega) - \sigma(0)$ is proportional to $\omega^s$, with $0 < s < 1$, over a wide frequency range. The $s$-parameter of this power-law response is consistent with the basic definition of the log-log slope, $s$, defined by $s \equiv d\ \ln[\Delta\sigma(\omega)/\sigma_n]/d\ \ln[\omega/\omega_0]$. Here,

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$\sigma_n$ and $\omega_0$ are normalization constants of magnitude unity, and we shall use just "slope" to mean $s$ hereafter.

Power-law response with $s$ frequency independent was publicized by Jonscher and called universal dielectric response [3,4], but more recently it has been termed universal dynamic response [5], making it clearer that it may appear in the response of either non-conductors or conducting systems. Fractional power-law frequency response is actually implicit in the 1854 work of Kohlrausch on stretched exponential behavior [2]. Because the BP treatment involves mobile charges and leads to a frequency-response equation which combines ac and dc response so that the dc response is just the zero-frequency limit of the ac response, it is an instance of what has been called conductive-system dispersion (CSD) [6,7]. By contrast, for dielectric-system response, the dominant ac behavior arises from dipoles or from relatively localized charges which are unable to percolate throughout the material, and a separate treatment is required to describe any dc response present. When such dielectric response shows dispersion, it is an instance of dielectric-system dispersion (DSD).

Unfortunately, the BP claims do not withstand detailed examination. First, these authors did not recognize and state that their final response equations (their Eqs. (9) and (10)) were instances of the transient and frequency response arising from a zero-mean Gaussian distribution of logarithmic relaxation times, which implies a Gaussian distribution of activation energies (actually enthalpies) in their thermally activated situation [8]. This is demonstrated analytically in the Appendix, but the analysis there also shows that the relaxation times appearing in the BP transient and frequency-response expressions are inconsistent with the simultaneous application of these equations to the same material. It is shown that a corrected calculation of the frequency response leads to a result which involves the same Gaussian distribution as that involved in the transient response. Finally, the actual expression for the relaxation time, $\tau_{BP}$, presented by BP is shown to be inappropriate for a conducting system.

Bondarev and Pikhitsa claim that the close agreement they present between the transient response predictions of their theory and that of stretched exponential response confirms the applicability of their theory for use in quantitative analysis of relaxation phenomena in disordered conductors. Their claim of "universal" frequency response is based on their demonstration that their theory can lead to frequency dependence of the power-law form mentioned above. But the majority of experimental data and most fitting models (including the KWW model at high relative frequencies) yield such response with $s$ frequency-independent over an appreciable frequency range, often extending for many decades. Unfortunately, a Gaussian-response model yields frequency-*dependent* $s$ response, with no actual non-zero-length frequency-response region involving constant-s behavior [8]. Furthermore, most frequency response dispersion data for conducting systems involve asymmetric response (such as that of the KWW and many other models) for complex-plane plots of $-\rho''(\omega)$ versus $\rho'(\omega)$, but the simplest Gaussian response model, that exemplified by the BP results, leads to completely symmetric response [8]. Thus, for both reasons the BP model is quite limited in the range of experimental data to which it may apply.

The BP approach involves averaging over random potential differences with a type of exponential distribution [1] but leads to final response associated with a Gaussian distribution of activation energies, perhaps an instance of the operation of the law of large numbers. A nuclear-magnetic-resonance response model involving a Gaussian distribution of barrier heights for ionic motion has been found to be useful for analyzing data in this area [9]. By contrast, the GBEM frequency-response model [10], a mean-field treatment of an effective-medium approximation, starts with a random-free-energy model having a uniform distribution but finally yields response which is quite close to that arising from the assumption of an exponential distribution of activation energies [11]. Finally, Dieterich and associates [12,13] have carried out Monte Carlo simulations of charged particles diffusing on a simple cubic lattice with local site energies taken as uncorrelated Gaussian-distributed random variables. These lattice-gas, Coulomb-interaction calculations led to approximate Cole–Cole [14] frequency response behavior at the dielectric level: $\epsilon(\omega) - \epsilon(\infty) \propto 1/[1 + (i\omega\tau_0)^\alpha]$, where $0 < \alpha \leqslant 1$, and $\alpha$ is frequency-independent. Thus, different assumptions about initial distributions can lead, not surprisingly, to quite different final

ones. It certainly remains to be shown, however, which assumptions yield best agreement with a variety of appropriate experimental data.

In spite of its limitations, the BP analysis is of some interest because it provides explicit expressions, in terms of microscopic quantities, of some of the various parameters which enter the Gaussian response model. Thus, in instances where data may be well fitted with this model, one can use estimates of the meso- and macroscopic fitting parameters to estimate values of some microscopic quantities involved in the BP Coulomb-fluctuation approach.

## 2. Parameters of the Bondarev–Pikhitsa Gaussian-response model

There are three fitting parameters involved in a Gaussian time or frequency response model. For frequency response they are: $\rho(0)$, the dc resistivity; $\tau_0$, a relaxation time which equals $1/\omega_p$, where $\omega_p$ is the frequency at the peak of the $-\rho''(\omega)$ response curve; and $\xi$, a measure of the width of the Gaussian distribution [7], being $\sqrt{2}$ times the standard deviation of the distribution. In the BP work, the related quantity $\nu \equiv \xi^2$ is used. According to the BP analysis, $\rho(0) = [\sigma(0)]^{-1} = \sigma_0^{-1} \exp(\xi/2)^2$, where they define $\sigma_0$ as the thermally activated conductivity of the system in the absence of disorder. Bondarev and Pikhitsa have expressed this $\sigma_0$ in the form

$$\sigma_0 = z^{-1} \exp(-E/k_B T), \tag{2}$$

where $E$ is the activation energy in the absence of disorder, $T$ is the absolute temperature, and $z$ is an undefined pre-exponential factor. A more explicit expression for $\sigma(0)$ was suggested for the exponential distribution of activation energies model [6,11]. If it is used to obtain $\sigma_0$, one has

$$\sigma_0 = (\epsilon_V/\tau_a)(E/k_B T)\left[\exp(E/k_B T) - 1\right]^{-1}, \tag{3}$$

where $\epsilon_V$ is the permittivity of vacuum; $1/\tau_a$ is a barrier-attempt phonon frequency; and $\tau_a$ is usually smaller than $10^{-12}$ s [15]. This expression not only involves the usual pre-exponential $1/T$ response, but it also reduces plausibly to the nearly temperature-independent quantity $\epsilon_V/\tau_a$ in the limit of small $E/T$.

Now BP also found that $\sigma(\infty) = \sigma(0) \exp(\xi^2/2)$ [1]. Recent work of the author [7,16] has demonstrated that for a dispersive, thermally activated, conductive system involving a distribution of relaxation times or, equivalently, activation energies, associated with physically realizable response, universal expressions for the low- and high-frequency limiting values of $\sigma(\omega)$ and $\epsilon_C(\omega)$ may be written in terms of the moments of the distribution. Here the subscript C denotes a quantity arising solely from the conducting-system response, omitting any dipolar contributions [7]. One of these universal expressions leads to the result $\sigma(\infty)/\sigma(0) = \langle(\tau/\tau_0)^{-2}\rangle / [\langle(\tau/\tau_0)^{-1}\rangle]^2$, equal to $\exp(\xi^2/2)$ for a Gaussian distribution, using the values of the moments of this distribution listed in the Appendix. Thus, the above BP expression is consistent with such a distribution, as one would expect. Incidentally, normalized moments of a distribution, such as $\langle(\tau/\tau_0)^{-1}\rangle \equiv \langle x^{-1}\rangle$, depend only on the shape of the distribution and involve only the variable $x \equiv \tau/\tau_0$, not $\tau_0$ separately.

Bondarev and Pikhitsa have defined their $\tau$ (used for either the $\tau_t$ or the $\tau_\omega$ of the Appendix) as

$$\tau_{BP} \equiv \epsilon_V \epsilon_\infty / \sigma_0, \tag{4}$$

where they define $\epsilon_\infty$ as the high-frequency dielectric constant. Since they do not discuss the CSD contribution to $\epsilon_\infty$ arising from mobile charges (see below), their $\epsilon_\infty$ will be interpreted herein as a dipolar DSD quantity and will be designated as $\epsilon_{D\infty}$. Thus, Eq. (4) connects the purely CSD quantity $\tau_{BP}\sigma_0$ with the purely DSD quantity $\epsilon_{D\infty}$. But this is a most implausible equation since it indicates that changes in $\epsilon_{D\infty}$, usually associated only with dipolar processes, result in direct changes in $\tau_{BP}\sigma_0$, CSD quantities associated with mobile charge motion. This problem has been discussed at some length recently [7], and it has been shown that the expression for the $\tau_0$ associated with a CSD process involves only CSD quantities, as one would expect. It should be emphasized, however, that a non-zero $\epsilon_{D\infty}$ will always be experimentally present (even in the absence of dielectric dispersion in the measured frequency range), and it will have an effect on the total measured response. But to at least first order, it will be an excellent approximation to calculate CSD response separately and then

include the effect of $\epsilon_{D\infty}$ as an independent part of the total response [6,7].

Recent work [7] leads to the universal conducting-system expressions

$$\tau_0 = [\epsilon_V \epsilon_C(0)/\sigma(0)\langle x\rangle] = [\epsilon_V \epsilon_C(\infty)\langle x^{-1}\rangle/\sigma(0)], \quad (5)$$

which become for a Gaussian distribution,

$$\tau_0 = [\epsilon_V \epsilon_C(0)/\sigma_0] = [\epsilon_V \epsilon_C(\infty)\exp(\xi^2/2)/\sigma_0], \quad (6)$$

on the introduction of $\sigma_0$ and the use of the values of the Gaussian moments listed in the Appendix. Eq. (6) is thus the necessary relation associated with the CSD response of a thermally activated material involving a Gaussian distribution and, therefore, should be used to replace Eq. (4). In addition, it should be set equal to the BP transient response relaxation time $\tau_t$ of Eq. (A.1). Finally, note that the Gaussian distribution imposes a ratio between $\epsilon_C(0)$ and $\epsilon_C(\infty)$ which depends on $\xi$. For the value of $\nu \equiv \xi^2 = 15.65$ used by BP, the ratio is about 2500.

Bondarev and Pikhitsa provide a complicated formula for $\nu$, which, however, is proportional to $1/\epsilon_{D\infty}T$. In view of the above considerations, such instances of $\epsilon_{D\infty}$ in the BP work should perhaps be changed to $\epsilon_C(0)$. When one neglects any $\epsilon_{D\infty}$ temperature dependence and takes the BP expression for the Debye length of the "plasma" of mobile defects proportional to $T^{1/2}$, it turns out that $\xi \propto T^{-1}$, so one expects the frequency width of such curves as $-\rho''(\omega)$ to increase as the temperature is lowered, usual experimental behavior. It is important to note that this temperature dependence for $\xi$ is the only one which allows a Gaussian distribution of activation energies to be temperature independent, the usual situation [8,11,17].

## 3. Model-fitting comparisons

To help evaluate the BP claims of universality and wide applicability for their model, it is useful to compare the predictions of that model with those of others. Luckily, an algorithm which allows one to calculate very accurately the frequency response arising from a Gaussian distribution has been a part of the readily available LEVM complex nonlinear least squares (CNLS) fitting program for several years [18] [2], and the current version also allows the associated transient response to be calculated correspondingly accurately. These procedures make it possible for one to fit experimental or synthetic data to the Gaussian response model very precisely, and their use will be demonstrated below in evaluating the appropriateness of the BP claims.

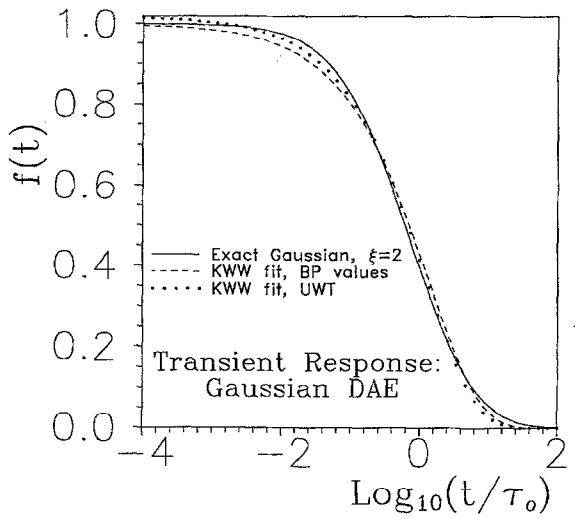


Fig. 1. Comparison of normalized transient response of the Gaussian model with KWW-model predictions using Bondarev–Pikhitsa fitting parameters and with the results of a unity-weighting nonlinear least squares KWW fit to the Gaussian data. Here, $\tau_0 = 1$ s.

### 3.1. Transient response

Because BP compared the transient response of their model to KWW response, it is worthwhile to consider how well a Gaussian response model can fit KWW synthetic data or vice versa. The following results were all calculated using the LEVM program and involved calculation of "exact" Gaussian or KWW data for fitting which had relative accuracies of $10^{-9}$. Fig. 1 shows the Gaussian $f(t)$ transient response of Eqs. (A.2) and (A.3) for $\tau_0 = 1$ s and

[2] The latest version of the LEVM fitting program may be obtained from Solartron Instruments; attention Dave Bartram; e-mail: bartram@solartron.com.

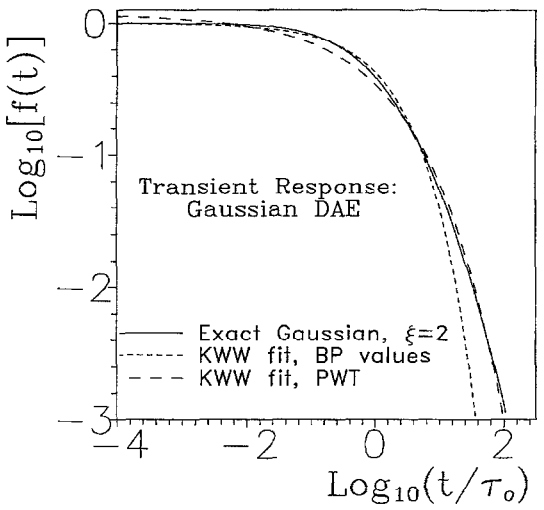


Fig. 2. Comparison of the logarithm of normalized transient response of the Gaussian model with that of KWW-model predictions using Bondarev–Pikhitsa fitting parameters and with the results of a proportional-weighting nonlinear least squares KWW fit to the Gaussian data.

$\xi = 2$, equivalent to the values used by BP. Also shown are two fits of these data, one using BP's KWW parameters: $f_K(0) = 1$, $\tau_K = \frac{4}{3}$ s, and $\beta = 0.58$, and the other obtained by unity weighting (UWT) [18] nonlinear least squares fitting of the Gaussian response data with the Eq. (1) model. The following parameter estimates were obtained from the latter fitting: $f_K(0) = 1.019$, $\tau_K = 1.195$ s, and $\beta = 0.601$. The $\tau_K$ value listed by BP was $\frac{3}{4}\tau_0$ [1], but $\frac{4}{3}\tau_0$ was actually used by these authors [19]. The BP fit results presented in their Fig. 2 are very close to those shown here, but BP only extended their curve down to $t/\tau_0 = 0.1$, thus omitting the short-time region where their fit curve diverges most from Gaussian response. Had they not done so, they might have modified their claim of close agreement between their response and KWW response.

But a better assessment of such agreement or disagreement may be obtained by plotting $\log[f(t)]$, rather than $f(t)$, versus $\log(t/\tau_0)$. Fig. 2 shows two of the same data sets of Fig. 1 plotted in this manner and, in addition, a proportional weighting (PWT) KWW fit of the Gaussian response. Here, 184 points extending from $t/\tau_0 = 10^{-4}$ to about 125 were used. The estimated parameters for this fit were $f_K(0) = 1.168$, $\tau_K = 0.603$ s, and $\beta = 0.382$. Note the large differences in some of these parameter values from those of the UWT fit. Such differences are an immediate indication that the KWW model is inappropriate for fitting Gaussian data.

Proportional weighting makes the relative residuals of the fit as equal as possible over the whole range. It is clear from the results shown in Fig. 2 that it yields much closer agreement in the high-frequency tail of the response than does the BP parameter set. Because Gaussian and KWW responses both reduce to single-time-constant Debye response as $\xi \to 0$, the degree of agreement between KWW and Gaussian response will increase as $\xi$ decreases, and vice versa. Thus, had the BP transient response comparisons been carried out using the larger value of $\xi$ that they employed for their frequency-response comparison, the discrepancies between the Gaussian and KWW model predictions would have been appreciably larger than those present in Figs. 1 and 2.

### 3.2. Frequency response

Both because BP compared their transient behavior with that of the KWW and because they state that "experimental data on non-Debye relaxation are usually fitted by the Kohlrausch function", it is useful to compare Gaussian and KWW response in the frequency domain as well as the time domain. Bondarev and Pikhitsa actually fitted their real-part Gaussian-model prediction of $\sigma'(\omega)$ to data for Na $\beta$-alumina at 113 K and found good agreement for a two-decade frequency range. An asymmetric fitting model was used earlier by the present author to fit this and data sets at other temperatures for this material [20], but here the emphasis will be on the adequacy of mutual fitting of Gaussian and KWW model data. First, it must be stressed that, as demonstrated below, model comparison using only real- (or imaginary-) part fitting is generally greatly inferior to full CNLS fitting of the real and imaginary parts of the data simultaneously. Similarly, fitting a model to experimental frequency-response data should also be carried out with full CNLS fitting.

First, 121 points of exact Gaussian data with frequency range from 0.01 to $10^{10}$ Hz were produced using the BP-fit $\beta$-alumina parameter values $\sigma(0) = 2.51 \times 10^{-7}(\Omega\ \mathrm{cm})^{-1}$ and $\nu = 15.65$. Thus, $\xi \simeq 3.956$, and a value of the $\tau_0$ of Eq. (A.8) of

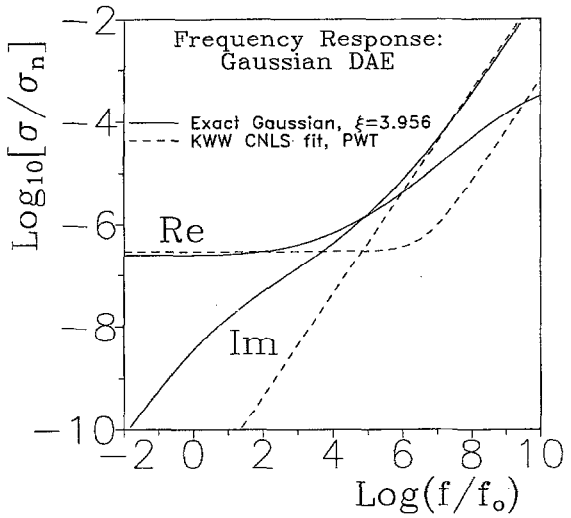


Fig. 3. Comparison of exact Gaussian-model frequency response with the results of a CNLS fit of the data with an approximate KWW response model using proportional weighting. Here and hereafter, $\sigma_n = 1\ (\Omega\ \mathrm{cm})^{-1}$ and $f_0 = 1$ Hz.

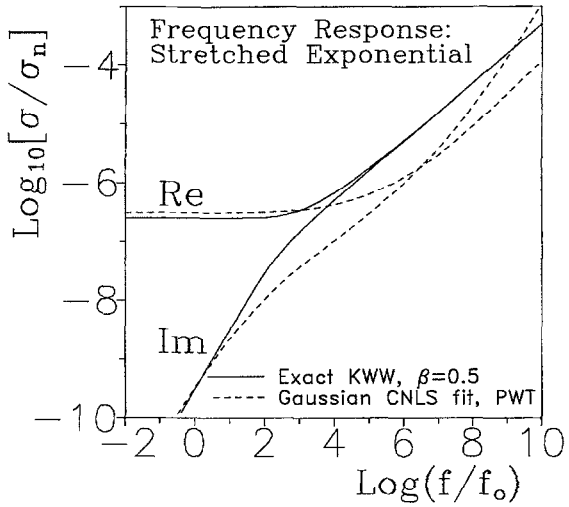


Fig. 4. Comparison of exact $\beta = 0.5$ KWW frequency response with the results of a CNLS fit of the data with an accurate Gaussian response model using proportional weighting.

$10^{-4}$ s was used. Because the distribution of relaxation times for KWW response is only known exactly in closed form for $\beta = 0.5$ [21] [3], making the calculation of accurate KWW frequency response for arbitrary $\beta$ very difficult [7,22], the above data were initially fit using an approximate KWW frequency-response algorithm [22] included in the LEVM CNLS fitting routine. Results for PWT CNLS fitting are presented in Fig. 3, and the parameter estimates obtained were about $\sigma(0) = 2.96 \times 10^{-7}(\Omega\ \mathrm{cm})^{-1}$, $\tau_0 = 2.36 \times 10^{-6}$ s, and $\beta = 0.989$! It is clear that both the real and imaginary fits are very poor. They are, however, much improved when each fit is carried out separately. Then the separate real and imaginary fit estimates of $\beta$ were found to be about 0.47 and 0.57, respectively. None of these values are arbitrary: they represent the optimum least squares estimates for the conditions considered.

Because the approximate KWW fitting model used above becomes less accurate at low relative frequencies, it was decided to reverse the above procedure and fit exact $\beta = 0.5$ KWW calculated frequency response with the accurate Gaussian response model. In generating the exact KWW data, the same $\sigma(0)$ and $\tau_0$ values as above were used. Fig. 4 shows the

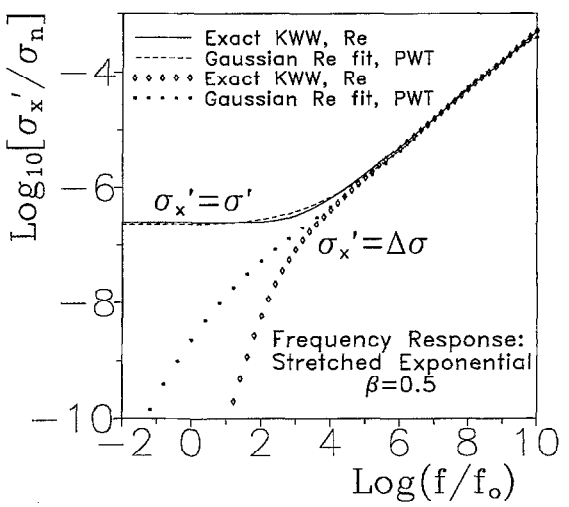


Fig. 5. Comparison of exact $\beta = 0.5$ KWW-model, $\sigma'(\omega)$ frequency response with the results of a CNLS fit of the data with an accurate Gaussian response model using proportional weighting. Both $\sigma'(\omega)$ and $\Delta\sigma(\omega) = \sigma'(\omega) - \sigma(0)$ response curves are shown.

[3] The lower limits of the integrals in Eqs. (9.1)–(9.4) of Ref. [21] should be $-\infty$, not 0.

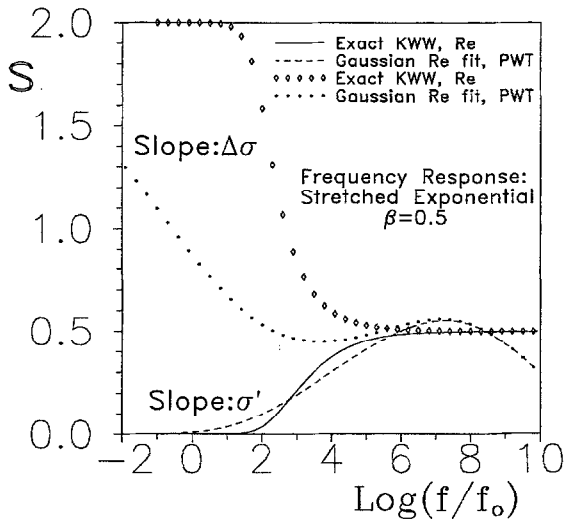


Fig. 6. Slopes, $s$, of the curves of Fig. 5.

CNLS fit results: still very poor. But Fig. 5 presents the PWT fit of the real part only, an apparently good fit with parameter estimates of $\sigma(0) = 2.31 \times 10^{-7}(\Omega\ \mathrm{cm})^{-1}$, $\xi \simeq 4.066$, and $\tau_0 = 1.44 \times 10^{-4}$ s. This generally good agreement between the fit and the model is comparable to that found by BP for their real-part Na $\beta$-alumina fit. But the present results clearly show that such agreement alone is insufficient to allow one to conclude that full Gaussian response can be well fitted by the KWW model or vice versa. Thus, the BP claim that their theory is applicable for good quantitative analysis of disordered conductors must be unequivocally rejected for those that exhibit KWW response and for most other responses, even most of those that involve symmetrical behavior.

Also shown in Fig. 5 are the exact KWW- and Gaussian-fit results for $\Delta\sigma(\omega)$. They make the difference between these models in the low-frequency region very clear. But it can be made even clearer by plotting the slopes of the four curves of Fig. 5 versus frequency. Accurately calculated slopes for both $\sigma'(\omega)$ and $\Delta\sigma(\omega)$ are presented in Fig. 6 and show that there is appreciable difference between the real-part KWW and Gaussian predictions even in the higher-frequency range. The Gaussian low-frequency-limiting slope of $\Delta\sigma(\omega)$ is 2 and the high-frequency-limiting slope is 0, since as BP have shown, $\sigma(\infty)$ is a non-infinite constant even when $\rho(\infty) = 0$. The results shown in the figure clearly demonstrate that there is no non-zero-length frequency range where $s$ is constant for Gaussian response. But for noisy data fitted over a limited frequency range, it can, nevertheless, sometimes be difficult to distinguish Gaussian response from that with a constant slope [8].

Note that the KWW $\Delta\sigma(\omega)$ slope properly approaches a value of 2 at low frequencies and the value of $\beta$ ($= 0.5$) at the high end [2,23]. The latter response is non-physical, however, if it extends indefinitely because it would then lead to infinite conductivity in this limit [23]. It is therefore necessary to cut off the KWW distribution at some small $\tau$ value [7]. Such a cutoff, whose effects often appear well beyond the range of usually measured frequencies, leads to a limiting high-frequency slope of 0 and thus to $\sigma(\infty) < \infty$. For simplicity, no cutoff effects are included herein.

It is interesting that exact Gaussian response with the above parameter values leads to the large value of $\epsilon_C(0) \simeq 1.4 \times 10^4$ and to $\epsilon_C(\infty) \simeq 5.7$. Neither quantity was recognized or included in the BP work. Thus, it is important to emphasize that $\epsilon_C(\infty)$ is an intrinsic part of CSD response and is unrelated to $\epsilon_{D\infty}$. In general, $\epsilon(\infty) = \epsilon_C(\infty) + \epsilon_{D\infty}$ [7]. The exact $\beta = 0.5$ KWW model with the same parameter values used above and without cutoff leads to $\epsilon_C(0) \simeq 567$ and to $\epsilon_C(\infty) = 0$. The cutoff value may be adjusted to make the KWW $\epsilon_C(\infty)$ comparable to the Gaussian value. No cutoff is needed for the Gaussian distribution because of the rapid decrease of its response away from the peak region. Limiting epsilon values may be calculated as in Eq. (5) from the value of $\sigma(0)$ and the moments of the appropriate distribution when it is known. When the distribution is unknown, the averages may be determined directly using LEVM fitting [6].

The present limiting high-frequency $s = 0.5$ KWW behavior is just an indication that even for data which are well fitted by the KWW model over an appreciable frequency range, one should not necessarily expect a low-frequency model to continue to apply as the frequency approaches phonon frequencies. In fact, Petersen and Dieterich [13] mention that it is a general property of lattice gas models that $\sigma(\infty)$ must be $< \infty$. Both the Gaussian response

model and the GBEM model satisfy this condition, as does KWW response derived from a cut off distribution [7]. A plateau in Na $\beta$-alumina $\sigma'(\omega)$ response in fact appears near $10^{10}$ Hz [24].

In order to demonstrate the differences between the basic Gaussian and KWW CSD responses alone without other perturbations, the comparisons presented in the present figures do not include any contribution from a non-zero $\epsilon_{D\infty}$. It is therefore useful to summarize what happens when such a $\epsilon_{D\infty}$ is included. To do so, a new exact KWW data set was prepared which was identical to that discussed above except that $\epsilon_{D\infty}$ was taken as 5 rather than zero. Full CNLS fitting of these data with the Gaussian model led to worse real-part agreement than that shown in Fig. 4 but to appreciably better imaginary-part agreement. In particular, the Gaussian-fit $\sigma''$ response exhibited the correct slope of unity at low frequencies and approached the same proper slope at high frequencies, with principal deviations appearing in the middle region. Neither full complex fitting nor imaginary-part fitting with $\epsilon_{D\infty}$ taken as a free parameter allowed a meaningful estimate of this quantity to be obtained, however. The reason is that when fitting Gaussian response to non-Gaussian data involving $\epsilon_{D\infty}$ the Gaussian parameters adjust themselves to yield an estimate of $\epsilon_C(\infty)$ as close as possible to the value of $\epsilon_{D\infty}$. Of course, when the Gaussian model is fitted to low-noise or to appreciably noisy Gaussian data involving a non-zero $\epsilon_{D\infty}$, full CNLS fitting can yield a good estimates of $\epsilon_{D\infty}$ even when it is much smaller than $\epsilon_C(\infty)$.

## 4. Conclusions

The Bondarev–Pikhitsa conductive-system response model is just that of a material with a simple Gaussian distribution of activation energies.

The relaxation times which appear in the BP quadrature expressions for transient and for frequency response are inconsistent; the source of the error is identified; and the inconsistency corrected.

The BP expression for their basic relaxation time in terms of other model parameters is physically implausible and inappropriate; a correct, purely conductive-system expression is provided; and the distinction between mobile-charge and dipolar contributions to the total high-frequency dielectric constant, one not recognized in the BP work, is elucidated.

The BP claims that their dispersion-model treatment provides closed expressions for the "universal" response functions of disordered ionic materials "and allows one to give a complete quantitative description of a large number of experimental data on the relaxation dynamics of disordered conductors", are unjustified. Not only does the simple Gaussian distribution of the BP theory lead only to loss-response symmetric about a peak, although most conductive-system data involve asymmetric response, but also it does not lead to power-law frequency response with a log-log slope independent of frequency over an appreciable range, the definition of universal dynamic response.

## Appendix

In this appendix, it will be shown that the BP transient and frequency response results involve a Gaussian distribution of activation energies and that the $\tau$'s which appear in their expressions for such response are mutually inconsistent. Thus, a correction is needed to enable their time and frequency response expressions to apply to the same material. Here, the limiting transient response as $t \to 0$, $f(0)$, is taken as unity since we shall deal with normalized distributions.

The BP dimensionless transient response result (their Eq. (9)) may be written as

$$f(t) = \pi^{-1/2} \times \int_{-\infty}^{\infty} du \exp\left[-u^2 - (t/\tau_t)\exp(\xi u)\right], \tag{A.1}$$

where their $\tau$ has been replaced by $\tau_t$ and their parameter $\nu$ by $\xi^2$. If $G(\tau)$ is a normalized distribution of relaxation times involving a constant relaxation time, $\tau_0$, then the corresponding normalized distribution of logarithmic relaxation times, $F(y)$, equals $\tau G(\tau)$, where $y \equiv \ln(\tau/\tau_0)$ [6–8]. The related distribution of activation energies is just $K(E) = F(y)/kT$, and for a log-normal $G(\tau)$, $F(y)$ and $K(E)$ are both Gaussian in form [7,8].

Since $f(0) = 1$ for Eq. (A.1), the underlying distribution involved in it must be normalized. Now the

general expression for the $f(t)$ response associated with $F(y)$ is [7,16,21,25,26] [4]

$$f(t) = \int_{-\infty}^{\infty} \mathrm{d}y F(y) \exp[-(t/\tau_0)\exp(-y)], \tag{A.2}$$

and the normalized $F(y)$ for the simplest zero-mean Gaussian distribution is [8]

$$F(y) = \pi^{-1/2}\xi^{-1} \exp\left[-(y/\xi)^2\right], \tag{A.3}$$

where $\xi$ is the breadth parameter of the distribution. Finally, when one substitutes Eq. (A.3) into (A.2) and then makes the substitution $u = -y/\xi$, it follows that the result is exactly the same as that of Eq. (A.1) when $\tau_t$ is set to $\tau_0$. Therefore Eq. (A.1), which BP characterized as an elegant formula, is not novel in form since it is just an expression for the transient response associated with a Gaussian distribution.

The unnormalized BP frequency response expression (their Eq. (10)) may be written at the complex resistivity level, after some rearrangement and the replacement of their i by $-$i, as

$$\rho(\omega) = \pi^{-1/2}\sigma_0^{-1} \int_{-\infty}^{\infty} \frac{\mathrm{d}u \exp\left[-(u^2 + \xi u)\right]}{1 + \mathrm{i}\omega\tau_\omega \exp(-\xi u)}, \tag{A.4}$$

where the BP $\tau$, here that which appears in their frequency response expression, has been renamed $\tau_\omega$. It follows when $\rho(\infty) = 0$, as is the case here, that

$$\rho(\omega)/\rho(0) \equiv I(\omega) = \pi^{-1/2} \int_{-\infty}^{\infty} \frac{\mathrm{d}u \exp\left\{-\left[u^2 + \xi u + (\xi/2)^2\right]\right\}}{1 + \mathrm{i}\omega\tau_\omega \exp(-\xi u)}, \tag{A.5}$$

where $I(\omega)$ is a normalized response function [6,7,10]. Now substitute $-v = u + \xi/2$ in Eq. (A.5). Then

$$I(\omega) = \pi^{-1/2} \times \int_{-\infty}^{\infty} \frac{\mathrm{d}v \exp(-v^2)}{1 + \mathrm{i}\omega\left[\tau_\omega \exp(\xi^2/2)\right] \exp(\xi v)}. \tag{A.6}$$

[4] The $G(\tau)$ and $\rho(\tau)$ functions defined in Ref. [26] are equivalent to the present $F(y)$ and $G(\tau)$ functions, respectively.

The general expression for $I(\omega)$ in terms of $F(y)$ is [6,7,16,25,26]

$$I(\omega) = \int_{-\infty}^{\infty} \frac{\mathrm{d}yF(y)}{1 + \mathrm{i}\omega\tau_0 \exp(y)}, \tag{A.7}$$

where the present $\tau_0$ must be the same quantity as that appearing in Eq. (A.2) when the same $F(y)$ distribution is used in both equations. Note that the moments of an arbitrary $F(y)$ distribution, $\langle(\tau/\tau_0)^n\rangle$, may be calculated by multiplying $F(y)$ in Eq. (A.7) by $(\tau/\tau_0)^n \equiv \exp(ny)$ and setting $\omega = 0$. It follows that the moments of the normalized Gaussian distribution of Eq. (A.3) are, for $n = \pm 2, \pm 1$, and 0, $\exp(\xi^2)$, $\exp[(\xi/2)^2]$, and 1, respectively.

Now substitute the Eq. (A.3) expression for $F(y)$ into Eq. (A.7) and let $v = y/\xi$. One then obtains

$$I(\omega) = \pi^{-1/2} \int_{-\infty}^{\infty} \frac{\mathrm{d}v \exp(-v^2)}{1 + \mathrm{i}\omega\tau_0 \exp(\xi v)}. \tag{A.8}$$

Comparison of Eqs. (A.6) and (A.8) shows that they are only identical when

$$\tau_\omega = \tau_0 \exp(-\xi^2/2) = \tau_t \exp(-\xi^2/2). \tag{A.9}$$

Thus, although the BP transient and frequency response results both involve a Gaussian distribution, the $\tau$'s present in their expressions are inconsistent except in the limiting $\xi = 0$ case. But it is clear that in order for their results to apply to the same material it is necessary that the $\tau_\omega$ of Eq. (A.4) be replaced by the Eq. (A.9) expression.

Although it is shown above that Eq. (A.8), not (A.6), is the normalized frequency response expression consistent with the transient response of Eq. (A.1), BP did not deal with distributions and formulas such as (A.2) and (A.7). Instead they used Fourier transforms to connect their $f(t)$ and $I(\omega)$ responses (see, eg., Ref. [7,21,25,26]), as in their Eq. (2). But these relations, in either Laplace or Fourier form, properly connect not $f(t)$, the basic transient relaxation function (often denoted as $\phi(t)$ [26]), but essentially [7,25,26] $-\mathrm{d}f(t)/\mathrm{d}t$ and $I(\omega)$. Since it turns out that their use with the $f(t)$ of Eq. (A.1) (with $\tau_t$ replaced by $\tau_0$), rather than with $-\mathrm{d}f(t)/\mathrm{d}t$, leads to the BP Eq. (10) in the form of Eq. (A.4) (with $\tau_\omega$ replaced by $\tau_0$), while transformation using $-\mathrm{d}f(t)/\mathrm{d}t$ yields the correct Eq. (A.8) result, the source of the error in Eq. (A.4) is evident.

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