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LETTER TO THE EDITOR

On the universal scaling of the dielectric relaxation in dense media

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Abstract. We reconsider the idea of the universal scaling of the α relaxation and point out what is the cause of the recent controversy concerning this concept. A necessary condition the scaling relationship has to follow is presented. Consequently, we suggest that a generalized scaling relationship, which is potentially able to account for the dielectric relaxation of low-molecular-weight as well as polymeric glass-formers, is likely to be established. The generalized scaling plot for the literature experimental data of several glass-forming systems (low molecular weight and polymeric) is presented.

Glass-forming systems have been the subject of continued interest for decades. However, despite the large number of experimental studies in numerous materials and much theoretical effort, there is still no satisfactory fundamental theory of the glass transition.

It is well established that the asymptotic frequency dependence of the loss component of dielectric susceptibility follows a common universal pattern for virtually all kinds of materials [1]

$$
\begin{aligned}
\varepsilon''(\nu) &\propto \nu^m & \text{for } \nu \ll \nu_p \\
\varepsilon''(\nu) &\propto \nu^{-n} & \text{for } \nu \gg \nu_p
\end{aligned}
\tag{1}
$$

where the parameters m and n ($0 \leqslant m \leqslant 1$, $0 \leqslant n \leqslant 1$) characterize the shape of the dielectric loss and ν_p is the maximum of the peak position. Such behaviour coheres with theoretical approaches which have been developed in order to establish a more fundamental physical picture of dielectric relaxation in condensed matter [2–4]. Along with the main power-law region above the peak in $\varepsilon''(\nu)$, which is described by n, the second power-law region, which is described by another exponent n', is often observed in dielectric loss of glass-formers.

Recently, a form of universality was discovered by Dixon *et al* [5], who found that the dielectric spectra of several low-molecular-weight glass-forming liquids can be collapsed onto a single scaling curve when plotted as $w^{-1} \log(\varepsilon'' \nu_p / \Delta \varepsilon \nu)$ against $w^{-1}(1 + w^{-1}) \log(\nu/\nu_p)$, where $\varepsilon'' = \varepsilon''(\nu)$ is the loss part of the dielectric susceptibility, ν the measuring frequency, $\Delta \varepsilon$ the relaxation strength, and w denotes the half-width of the loss peak normalized to the half-width of the Debye peak. Although the authors of [5] did not provide any theoretical underpinning, this scaling works amazingly well for many low-molecular-weight systems [5–9]. Moreover, even the high-frequency deviation (second power-law region above the peak in ε'') from the main characteristic is remarkably universal in terms of the scaling [5–7]. Since the DC conductivity at low frequencies or the β process at high frequencies may overlap the primary response, the precise determination of

the parameters $\{\Delta\varepsilon, \nu_p, w\}$ of the scaling is sometimes difficult. There has been also some controversy concerning the correct subtraction of the DC conductivity [5, 9] (nevertheless the argument is given in [9] that the subtraction of the DC conductivity does not strongly influence the slope of the low-frequency side of the spectrum). However, this procedure has become extensively applied to the analysis of the dielectric response in glass-forming liquids [5–10]. The scaling expression has been used to argue that the static susceptibility diverges in supercooled liquids [7].

On the other hand, the concept proposed in [5] has been criticized by a number of authors. Schönhals *et al* [9] have pointed out that the validity of the scaling relationship is restricted to the relaxation which follows the power-law rules with $m \simeq 1$ and $w \simeq n^{-1}$, and it fails at low frequencies when $m < 1$. The great majority of low-molecular-weight glass-forming liquids follows the behaviour with $m \simeq 1$; however the behaviour with $m < 1$ is also reported [11, 12]. For polymeric systems, the latter type of relaxation is often reported [13]. Chamberlin [8] has proposed a modified scaling relationship for the systems characterized by the Curie–von Schweidler (CvS) relaxation function $\Phi(t) \propto (t/\tau)^{-\alpha}$ ($0 < \alpha < 2$; τ is the relaxation time). This situation may suggest that the half-width of the peak as the shape parameter is insufficient for the scaling in a wider class of materials and generally two shape parameters are required.

Kudlik *et al* [12] have reported precise measurements of the dielectric loss in several low-molecular-weight glass-formers, which show systematic discrepancies when plotted on the scaling master plot suggested in [5]. In view of this finding, Leheny *et al* [14] have proposed a new interpretation of the scaling procedure (for the original interpretation see figure 1 of [7] and explanations therein) and state that 'each spectrum scales through the optimization of three parameters—w, $\Delta\varepsilon$ and ν_p'. However, neither the method of optimization of these parameters nor the reference curve against which to fit the data has been given. Accordingly, no relationship which expresses the universality suggested in [5] is known at the moment. The key question becomes whether such a relationship exists in any case.

In this paper we show that the universality implied in [5] can be expressed in terms of well defined parameters. Moreover, it can be generalized to account for the relaxation of the low-molecular-weight and polymeric systems which follow the behaviour with $m < 1$.

Figure 1 shows a typical dielectric loss peak along with the curves representing the power-law rules (1), for the low- ($\nu \ll \nu_p$) and high-frequency ($\nu \gg \nu_p$) limits (the latter refers to the first power-law region above the peak in ε''). Evidently, these characteristics are linear when plotted in a double-logarithmic plot (as in the inset to figure 1). The parameter m determines the slope of the low-frequency characteristic and $-n$ the slope of the high-frequency one. The characteristic frequency ν_s and dielectric loss ε_s are defined as the frequency and dielectric loss corresponding to the intersection of these characteristics. We show that the scaling relationship suggested in [5] can be rationalized when considering a pair of power-law characteristics instead of the loss peak itself. At the level of generality we are working with, we have decided to apply mathematical models of the relaxation rather than experimental data, to illustrate the considerations.

First of all, we consider the relaxation showing the behaviour with $m \simeq 1$. The scaling suggested in [5] is restricted strictly to this case. In the frequency domain, this kind of relaxation is well described in terms of the Cole–Davidson (CD) empirical form, according to which the complex dielectric susceptibility $\varepsilon^*(\nu)$ is given by

$$\frac{\varepsilon^*(\nu) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \left(1 + \frac{i\nu}{\nu_0}\right)^{-n} \tag{2}$$
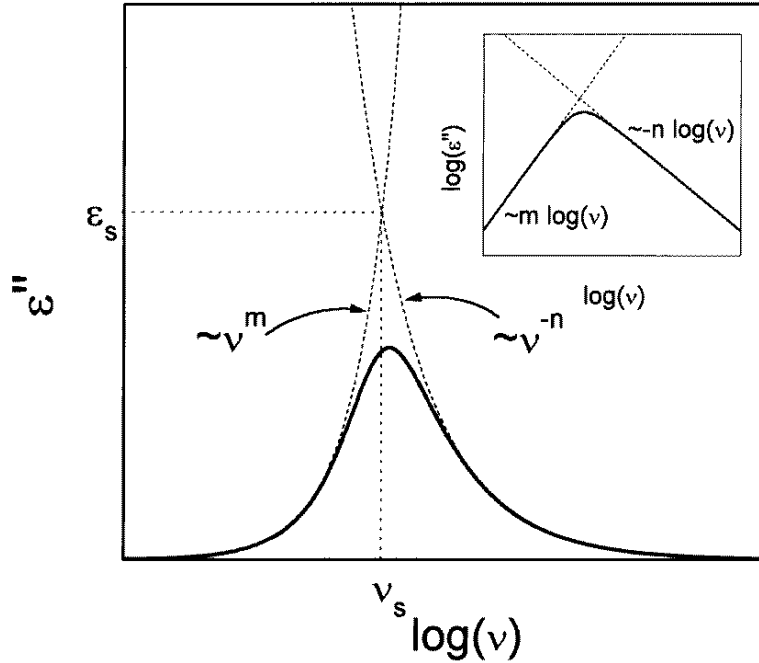
Figure 1. The frequency dependence of the dielectric loss ε''. Dashed lines represent the power law rules $\varepsilon'' \propto \nu^m$ and $\varepsilon'' \propto \nu^{-n}$. Characteristic frequency ν_s and characteristic absorption ε_s are determined by the intersection of the two power-law characteristics. The inset shows the frequency dependence of ε'' in a double-logarithmic photo.

ε_0 and ε_∞ are the relaxed ($\nu = 0$) and unrelaxed ($\nu = \infty$) dielectric susceptibility values, ν_0 is the frequency related to the relaxation time $\tau = (2\pi \nu_0)^{-1}$, and $i = \sqrt{-1}$. It is evident that this form follows (1) with $m = 1$. The natural idea as to how to create the scaling plot is to normalize ν by ν_s and ε'' by ε_s. Figure 2(a) shows three dielectric loss curves generated by (2) (with the half-width of the peaks ranging between 1.14 and 2.12) normalized this way. The next step is the division of $\varepsilon''/\varepsilon_s$ by ν/ν_s as in the original proposition. Lastly, multiplication of the logarithm on the horizontal axis by a factor of $(1 + n)$ results in a common curve at high frequencies. Figure 2(b) shows the loss curves generated by (2) virtually collapsed onto a single scaling curve. The abscissa of the scaling plot is $(1 + n)\log(\nu/\nu_s)$ and the ordinate is $\log(\varepsilon'' \nu_s / \varepsilon_s \nu)$.

The good job done by the scaling form proposed by Dixon *et al*, as reported in a series of experimental studies [5–8], is no surprise in the light of this finding. As long as the relaxation follows $m = 1$ and $w \simeq n^{-1}$, the form proposed here is analogous to the kernel of the form suggested in [5]. One realizes that the parameters ν_s and ε_s are analogous to their counterparts ν_p and $\Delta \varepsilon$ from the original proposition. The parameter n refers to the first power-law region above the peak in $\varepsilon''(\nu)$, as for w. However, apart from the Debye relaxation (when one can easily show that $\nu_s = \nu_p$, $\varepsilon_s = \Delta \varepsilon$ and $n = w^{-1} = 1$; both scaling forms become identical) we cannot adjudicate whether or not the parameters ν_s and ε_s are strictly equal to ν_p and $\Delta \varepsilon$, since the actual susceptibility function remains unknown.

The meaning of the additional factor w^{-1} which appears in the abscissa and the ordinate of the form suggested in [5] is illustrated in the insets to figure 2. The bottom left-hand
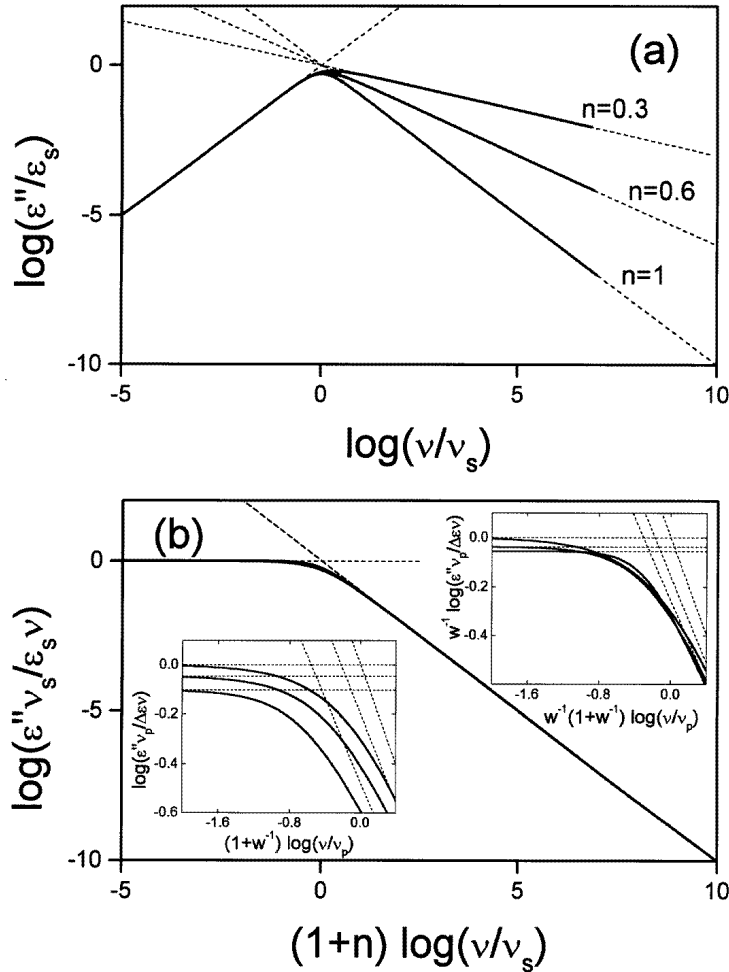
Figure 2. (a) The dielectric loss curves generated from the CD function, for selected values of the parameter n, normalized by plotting $\log(\varepsilon''/\varepsilon_s)$ against $\log(\nu/\nu_s)$. Dashed lines represent the power-law characteristics. (b) The same loss curves plotted as $\log(\varepsilon''\nu_s/\varepsilon_s\nu)$ against $(1+n)$ $\log(\nu/\nu_s)$. The insets show the meaning of the factor w^{-1} for both the abscissa and the ordinate of the scaling form proposed in [5].

inset shows the loss peaks from the main plot of figure 2, plotted as $\log(\varepsilon''\nu_p/\Delta\varepsilon\,\nu)$ against $(1+w^{-1})\log(\nu/\nu_p)$ (the kernel of the original expression) while the top right-hand inset shows them plotted as $w^{-1}\log(\varepsilon''\nu_p/\Delta\varepsilon\,\nu)$ against $w^{-1}(1+w^{-1})\log(\nu/\nu_p)$ (the full expression proposed in [5]). Evidently, multiplication of both the abscissa and the ordinate by the same factor is not able to influence the slopes of the linear parts of the master plot. However, this factor reduces the discrepancies that inevitably occur when the scaling is formulated in terms of the parameters $\{\Delta\varepsilon,\ \nu_p,\ w\}$. The kind of discrepancy observed in the top right-hand inset to figure 2 substantially agrees with that reported by Kudlik *et al* [12] for several low-molecular-weight glass-forming liquids, in the central and low-frequency region of the scaling plot (see figure 2 of [12]).

As regards the recent interpretation of the scaling procedure given in [14], the above

considerations gives the unique definition of the scaling parameters $\{\Delta\varepsilon, v_p, w\}$ (in contrast to the approach proposed in [14]). One realizes (see figure 2(a)) that any other definition of the parameters of the original scaling form except $v_p \equiv v_s$, $\Delta\varepsilon \equiv \varepsilon_s$ (see the insets to figure 2(b)) and $w \equiv n^{-1}$ inevitably results in discrepancies on the scaling diagram. Accordingly, the above statement provides a necessary condition the scaling procedure has to follow, assuming power-law limiting behaviour below and in the first region above the peak in ε''. Surprisingly, the loss curves generated by (2) follow a simpler scaling pattern than that originally proposed in [5], with no additional factor for both axes. This is contrary to the original expression where the additional factor w^{-1} for both axes appears.

Applying the analogous scheme, we consider the more general case of relaxation showing low-frequency behaviour with $m \leqslant 1$. The natural way of describing this type of relaxation in terms of the power-law rules is the Dissado–Hill (DH) susceptibility function [2], which reads

$$\frac{\varepsilon^*(v) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \left(1 + \frac{\mathrm{i}v}{v_0}\right)^{-n} \frac{{}_2F_1(n,\, 1-m,\, 1+n;\, [1+\mathrm{i}(v/v_0)]^{-1}}{{}_2F_1(n,\, 1-m,\, 1+n;\, 1)}. \tag{3}$$

The notation ${}_2F_1$ represents the Gaussian hypergeometric function [15], while m and n are line shape parameters which fulfil (1). The DH theory relates the parameters m and n to the energy redistribution within and among clusters. The mathematically equivalent susceptibility function was developed by Schönhals and Schlosser [3] from the considerations of damped diffusional propagation of conformational orientation along the polymer chains. It can be analytically shown [2, 15], that when $m = 1$ (3) reduces to (2).

Figure 3(a) shows three dielectric loss curves generated by (3) for selected values of $0.5 \leqslant m \leqslant 1$ and $0.2 \leqslant n \leqslant 1$ (the unnormalized half-width of the ε'' peak ranges between 1.14 and 3). Applying a scheme analogous to that described above, we come to the generalized scaling relationship. Figure 3(b) shows the loss curves generated by (3) virtually collapsed onto a single scaling curve. The abscissa is $(1 + n/m)\log(v/v_s)$ and the ordinate is $m^{-1}\log(\varepsilon'' v_s^m/\varepsilon_s v^m)$. It is evident that when $m = 1$ the above scaling form reduces to that developed previously in this paper. The bottom left-hand inset to figure 3(b) shows to what degree the data generated from (3) are collapsed (the differences are about 0.02 of the unit on the vertical axis of the scaling plot). The top right-hand inset shows the scaling behaviour of the susceptibility function derived from the CvS relaxation function, the well known Havriliak–Negami (HN) susceptibility function ($\varepsilon^*(v) \propto (1 + (\mathrm{i}v/v_0)^m)^{-n/m}$), and the Debye function (a special case of both HN and DH expressions for $m = n = 1$) as a reference curve. Apparently, apart from the central region of the scaling plot, where considerable discrepancies occur, all presented curves have a common scaling plot.

Figure 4 presents the experimental dielectric spectra of four glass-forming liquids (two low-molecular-weight and two polymeric glass-formers) taken from [16] on the common scaling plot proposed in this paper. The data are for salol (van der Waals liquid), glycerol (hydrogen bonded liquid), polymethylacrylate (PMA) (side group polymer), and polyethyleneterephthalate (PET) (main chain polymer). Within the limits of the accuracy of the measurements, all the data are collapsed onto a single scaling curve. Moreover, the high-frequency deviation from the power-law behaviour also tends to be universal for different samples. The top right-hand inset is the magnification of the central (nonlinear) region of the scaling plot (the solid line represents the HN fit to the data for PET, $m = 0.75$, $n = 0.28$), while the bottom left-hand inset shows the same data on the original scaling plot suggested in [5].

In this letter we discuss some of the formal aspects of the scaling approach which must be understood in order to clear up the cause of the recent controversy concerning
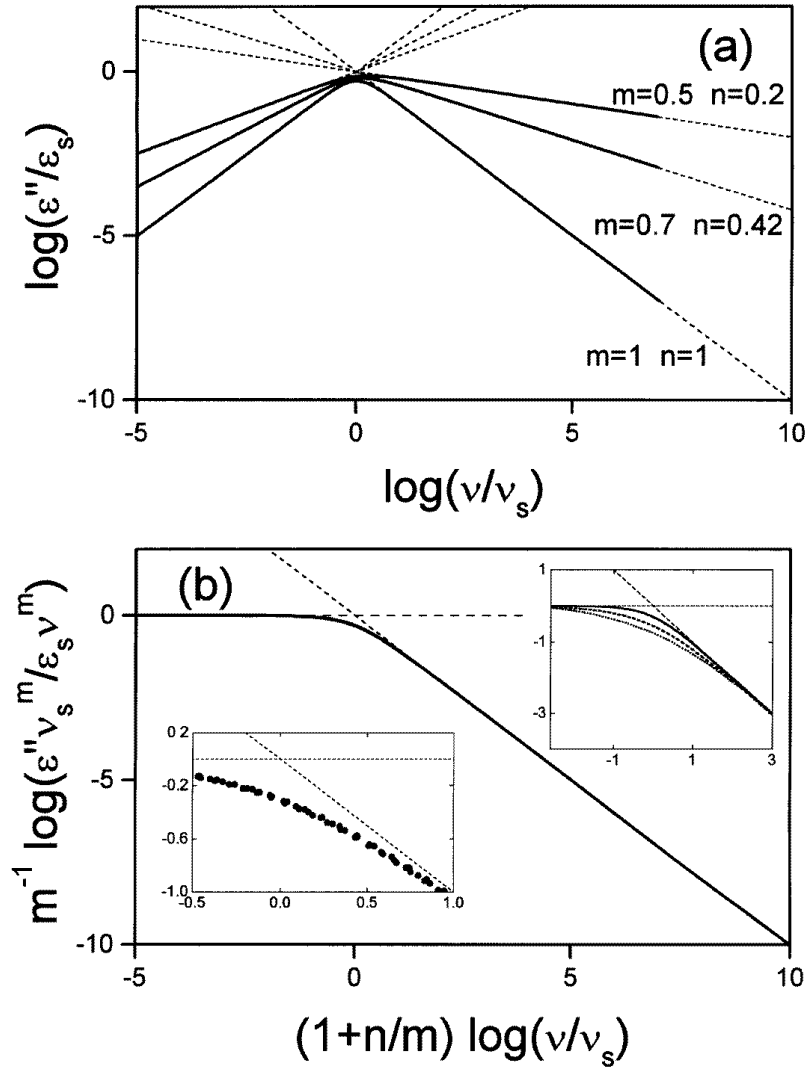
Figure 3. (a) The dielectric loss curves generated from the DH function, for selected values of the parameters m and n, normalized by plotting $\log(\varepsilon''/\varepsilon_s)$ against $\log(\nu/\nu_s)$. Dashed lines represent the power-law behaviour. (b) The same loss curves plotted as $m^{-1}\log(\varepsilon''\nu_s^m/\varepsilon_s\nu^m)$ against $(1+n/m)\log(\nu/\nu_s)$. The bottom left inset shows to what degree the generated loss curves are collapsed in the nonlinear part of the scaling plot. The top right inset shows the scaling behaviour of the susceptibility function derived from the CvS relaxation function ($\alpha = 0.8$, dotted line), the HN susceptibility function ($m = 0.7$, $n = 0.42$, dashed line) and the Debye susceptibility function (a special case of both HN and DH expressions for $m = n = 1$, solid line).

this concept [12, 14] and to make possible further progress in this matter, towards either confirming or denying the hypothesis of the universal scaling. We show that the scaling procedure proposed in [5] can be rationalized and regarded as the approximation of the simpler relationship formulated in terms of the parameters $\{\varepsilon_s, \nu_s, n\}$ instead of $\{\Delta\varepsilon, \nu_p, w\}$. The scaling relationship formulated this way has a mathematical form analogous to
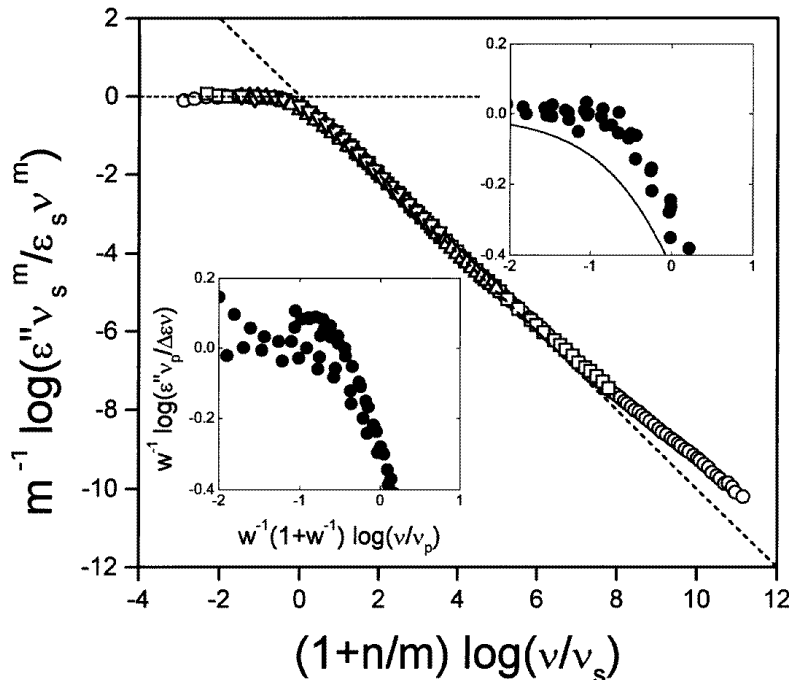
Figure 4. Dielectric loss data for a collection of glass-forming liquids, taken from [16], replotted on the scaling plot $m^{-1}\log(\varepsilon'' v_s^m/\varepsilon_s v^m)$ against $(1+n/m)\log(v/v_s)$. The data are for salol ($\square$, 233 K, van der Waals liquid), glycerol ($\bigcirc$, 333 K, hydrogen bonded liquid), polymethylacrylate (PMA) ($\triangledown$, 313.2 K, side group polymer), and polyethyleneterephthalate (PET) ($\triangle$, 358 K, main chain polymer). The top right inset shows a magnification of the nonlinear region of the main plot; the solid line represent the HN fit to the data for PET. The bottom left inset shows the data from the main plot plotted according to the original scaling relationship proposed in [5].

the original one; however the additional factor w^{-1}, which appears in the abscissa and the ordinate of the original expression, does not appear in the present one. We show that this factor acts to reduce the discrepancies which the original procedure inevitably produces. The formulation presented provides a unique definition of the scaling parameters (no prescription is known for the optimization mentioned in [14]). Moreover, it can be naturally generalized for the case of more complex systems which follow the behaviour with $m < 1$. The generalized relationship incorporates four parameters $\{\varepsilon_s, v_s, m, n\}$.

The suggested relationship cannot be regarded as a mathematical property of the DH susceptibility function (see the bottom left-hand inset to figure 3(b)) or any other function we have investigated (the top right-hand inset to figure 3(b) shows the scaling plot for a few of them; see also the top right-hand inset to figure 4). Instead, this approach provides the description of the shape of the loss spectrum in the vicinity of the peak, which differs from those already presented in the literature. We show that v_s is the only definition of the central frequency of the loss peak which is coherent with the scaling approach (neither v_p nor v_0 of any fitting form we have investigated exhibits this property, contrary to the suggestions in [14]).

The parameters m and n of the procedure presented relate the concept of the universal scaling to the more sophisticated microscopic interpretation [2, 3] based on the concepts

of the cooperative dielectric response and propagation of the conformational orientation in polymer chains. Evidently, verification of the universality suggested in [5] still requires experimental studies.

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