Response of Disordered Matter to Electromagnetic Fields

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We have studied a variety of different disordered materials, including molecular and ionic liquids, supercooled liquids, glasses, ionic conductors, and doped semiconductors, in ac electromagnetic fields over an exceptional broad dynamic range, including the rarely investigated GHz to THz region. All classes of disordered matter exhibit an astonishingly similar response: In addition to Jonscher's time-honored "universal dielectric response," a superlinear power-law increase of the frequency-dependent conductivity shows up bridging the gap between the classical dielectric and the infrared region. Thus the universal dielectric behavior of disordered matter extends up to much higher frequencies than thought until now.

Disordered matter is ubiquitous in our daily lives. Its electrical applications are numerous; e.g., the use of doped semiconductors as standard materials for electronics, glasses and polymers as insulator materials, or ionic conductors for accumulators and fuel cells. Because an increasing number of devices (e.g., in wireless communication or computer techniques) operate at progressively higher frequencies, the knowledge of the response of disordered matter to electromagnetic ac fields, in as broad a frequency range as possible, is of high technical relevance. However, the ac response of disordered matter is also interesting from a theoretical point of view, especially since a number of universalities were found in such different materials as, e.g., supercooled liquids and doped semiconductors [1–5]. Also, in mechanical relaxation experiments, the universal behavior of disordered matter was observed a long time ago (see [6]). Thus far, these universalities are restricted to certain classes of materials and/or limited frequency regimes. There is very little information about the important, but difficult to access, frequency region between the range of classical dielectric spectroscopy ($\nu < $ GHz), and the infrared (IR) region. In a time-honored review article, Jonscher [1] demonstrated that the ac response of disordered matter to electromagnetic fields at $\nu < $ GHz follows the so-called "universal dielectric response" (UDR), showing up as a sublinear power law in the frequency-dependent conductivity, $\sigma'(\nu)$. In some cases an additional linear or even superlinear increase of $\sigma'(\nu)$ was detected at higher frequencies and low temperatures [2–4,7–14]. In the present Letter, we show data on the electrical properties of dipolar, ionically and electronically conducting materials, measured over an extremely broad frequency range. We find that, in the full spectral range up to IR frequencies, *all* classes of disordered matter exhibit an astonishingly similar answer to electromagnetic fields, characterized by the succession of a sublinear and a superlinear power law (SLPL).

The response of matter to ac electrical fields is usually described in terms of the complex conductivity $\sigma^* = \sigma' + \sigma''$ or dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$. In the present Letter, $\sigma'(\nu)$ and the dielectric loss $\varepsilon''(\nu)$ are considered, both related by $\sigma' = 2\pi\nu\varepsilon''\varepsilon_0$ (ε_0 is the permittivity of free space). We performed measurements in an exceptionally broad frequency range by combining a variety of experimental techniques [13,15]. At low frequencies, electrode polarization plays a role, and in the present Letter only data are shown where electrode contributions can be excluded [16].

Supercooled liquids, becoming glasses at low temperatures, are classical examples of disordered matter. For dipolar supercooled liquids, recently the dielectric response up to IR frequencies was determined [12,13]. As an example, in Fig. 1 we show $\sigma'(\nu)$ of liquid and supercooled propylene carbonate (PC) [13]. The observed knees correspond to peaks in $\varepsilon''(\nu) \sim \sigma'(\nu)/\nu$ [Fig. 2(a)]. The position of these so-called α-relaxation peaks characterizes the dynamics of the dipolar molecules, closely related to the structural relaxation process, determining, e.g., the viscosity. Its temperature shift demonstrates the slowing down of the molecular motion at the glass transition [13]. The UDR regime is revealed at the high-frequency side of the relaxation peaks and, in many supercooled liquids including PC, can be identified with the so-called "excess wing" showing up as a second power law following the high-frequency flank of the α peak. It was recently demonstrated to be due to a second relaxation process of so-far unsettled origin [17], which in various other supercooled liquids leads to well-defined peaks at frequencies beyond the α peaks [18]. The lines through the curves of PC in Fig. 1 are fits with an empirical function describing the structural relaxation contribution [13], followed by the UDR, $\sigma' \sim \nu^s$ ($s < 1$). However, at high frequencies, fits and experimental curves deviate and a SLPL, $\sigma'(\nu) \sim \nu^n$, shows up (dashed line, $n = 1.6$). The superlinearity of $\sigma'(\nu)$ is best demonstrated plotting $\varepsilon''(\nu)$, where the UDR and SLPL regimes are separated by a well-defined minimum [Fig. 2(a)]. Beyond the minimum, $\varepsilon''(\nu)$ continues increasing towards IR frequencies where a peak shows up, usually
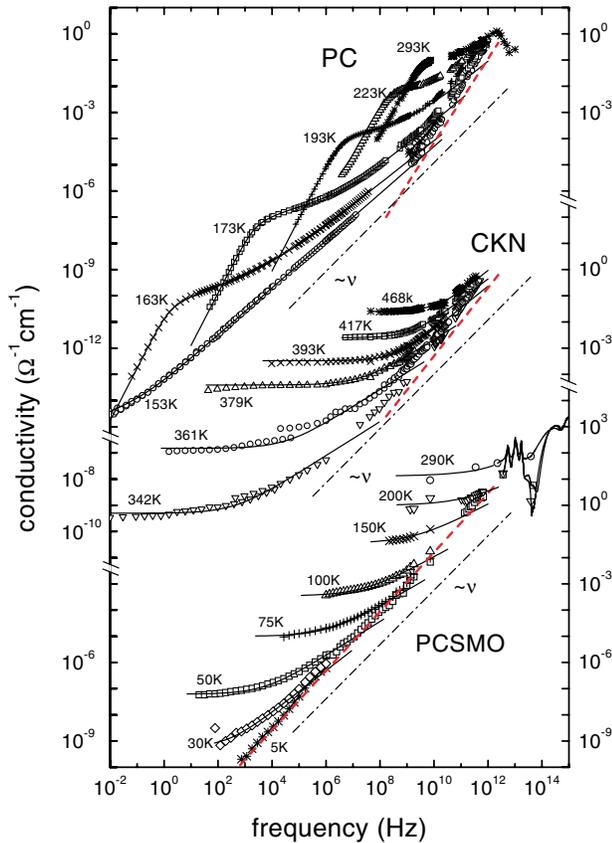
FIG. 1 (color online). Frequency-dependent conductivity at various temperatures for three different disordered materials. For the ionic conductor CKN and the electronic semiconductor PCSMO, the solid lines below THz indicate fits with the sum of dc conductivity and the UDR. For the dipolar system PC, the dc conductivity is replaced by a relaxation contribution. The dash-dotted lines demonstrate a slope of one. At high frequencies, a transition from UDR to a SLPL, indicated by the dashed lines, is observed.
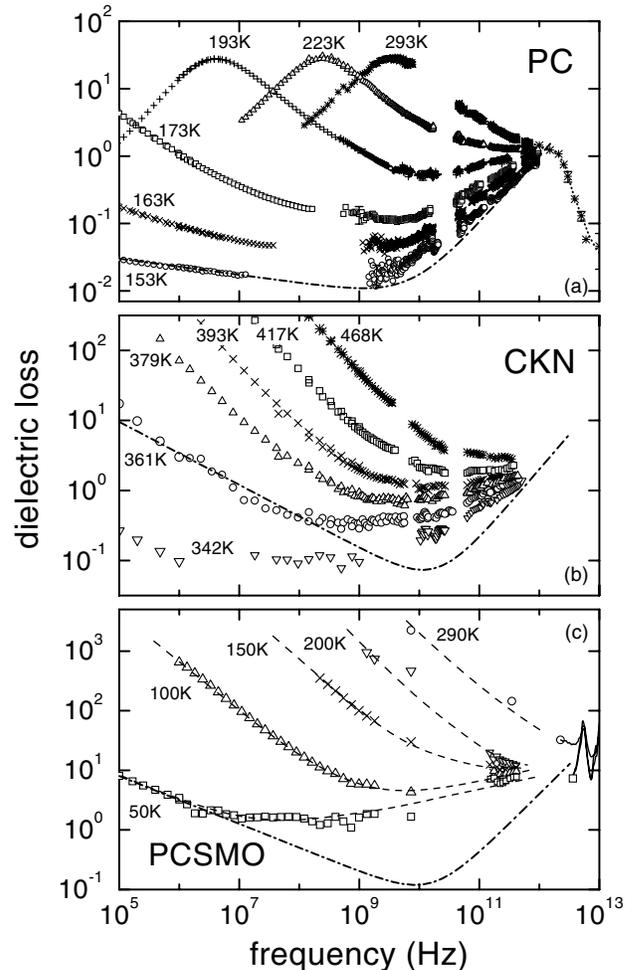

FIG. 2. Frequency-dependent dielectric loss for the same materials as in Fig. 1. The dashed lines are guides for the eyes. For PCSMO, the results in the THz region are shown as solid lines. The dash-dotted lines demonstrate that the shallow $\varepsilon''(\nu)$ minimum cannot be described by the sum of the UDR contribution and a linear increase towards the THz excitations.

termed "boson peak," with a characteristic frequency typical for vibrational excitations. This overall dielectric response of supercooled liquids is also shared by the so-called plastic crystals, where the molecules are disordered with respect to their orientational degrees of freedom [19].

In ionically conducting materials, the ac response is dominated by charge transport via hopping ions. As an example, we show the behavior of glass forming $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ (CKN) [10] [Figs. 1 and 2(b)]. Here the low-frequency response is dominated by dc contributions, showing up as a low-frequency plateau in $\sigma'(\nu)$, respectively, an initial ν^{-1} decrease in $\varepsilon''(\nu)$, which is followed by the UDR. For ionic conductors, the UDR is often ascribed to hopping conduction of the ionic charge carriers (see, e.g., [3,8,11]). The lines in Fig. 1 are fits with $\sigma' = \sigma_{dc} + \sigma_0\nu^s$. Again a SLPL of $\sigma'(\nu)$ is clearly revealed (dashed line, $n = 1.3$), leading to a shallow minimum in $\varepsilon''(\nu)$ [Fig. 2(b)]. A similar behavior was observed for other, not only glassy but also

crystalline, ionic conductors (see, e.g., [2–4,7–9,11]). In particular, in [2,9,11] a high-frequency transition to a nearly linear increase of $\sigma'(\nu)$, corresponding to a so-called "nearly constant loss" was reported. However, measurements extending up to sufficiently high frequencies or low temperatures indeed reveal a SLPL [3,7,8], leading to a shallow minimum in $\varepsilon''(\nu)$.

Finally, and rather unexpected, we found that also doped electronic semiconductors show a SLPL. We show results on a colossal magnetoresistance manganite, close to the metal-to-insulator boundary, namely, $Pr_{0.65}(Ca_{0.8}Sr_{0.2})_{0.35}MnO_{0.35}$ (PCSMO, Fig. 1) [20]. This material is especially suited due to its strong substitutional disorder. Again, at low frequencies we find a sequence of dc conductivity and UDR (solid lines). For doped and amorphous semiconductors, the UDR is usually ascribed to hopping conduction of Anderson-localized charge carriers [21] and theoretically explained, e.g., within Mott's variable-range-hopping

model [22]. For high frequencies, very similar to the behavior of supercooled liquids and ionic conductors, $\sigma'(\nu)$ smoothly passes into a SLPL extending towards THz frequencies (dashed line, $n = 1.13$). In $\varepsilon''(\nu)$, a shallow minimum shows up [Fig. 2(c)], followed in the IR region by sharp resonancelike phonon modes.

One of the very few examples of measurements in a similarly broad frequency range on electronic conductors is given in [23], where quite similar results were obtained for a polaronic semiconductor, including an increase of $\sigma'(\nu)$ steeper than linear at high frequencies. Further examples are given in Fig. 3. An interpolation between low- and high-frequency results reveals that, for CdF_2:In, a semiconductor with shallow donor states [24], a SLPL most likely is also present (dashed line, $n = 1.2$). The inset shows that indeed a shallow minimum of $\varepsilon''(\nu)$ is observed. The results on the single-crystalline Mott-Hubbard insulator $LaTiO_3$ demonstrate that the UDR and SLPL (dashed line, $n = 1.5$) also can be observed in systems with only marginal disorder. In this case, a slight off stoichiometry or impurities at a ppm level are sufficient to produce this typical response of disordered matter.
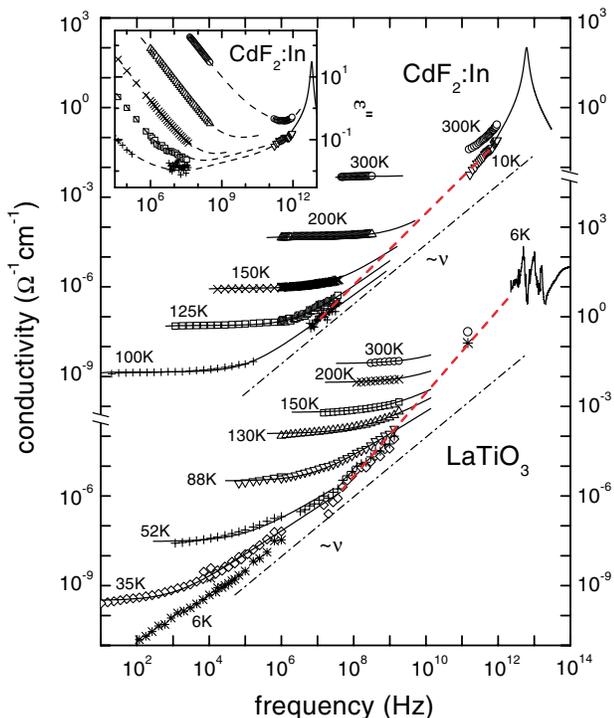
The unified view that can be condensed out of Figs. 1–3 is presented in Fig. 4, where we schematically show $\sigma'(\nu)$ and $\varepsilon''(\nu)$ for disordered matter. At the lowest frequencies, for materials with reorienting dipoles relaxational behavior shows up, while dc conductivity is observed for materials with free charge carriers. At higher frequencies, all classes of disordered matter show a succession of a sublinear power law at intermediate and an only weakly temperature-dependent SLPL at high frequencies, with the crossover frequency shifting upwards on increasing temperature. This behavior, indicated by the solid lines, can be identified even better by plotting the dielectric loss, where these two regimes are separated by a shallow minimum [Fig. 4(b)].

Concerning the origin of the SLPL, it clearly cannot be explained by a simple transition from UDR behavior to a quadratic or stronger frequency dependence, which can be assumed for the low-frequency flank of the microscopic excitations. This is demonstrated by the dash-dotted lines in Fig. 2, calculated by adding the UDR and a linear

FIG. 3 (color online). Frequency-dependent conductivity at various temperatures for semiconducting CdF_2:In [24] and $LaTiO_3$. The results in the THz region are shown as solid lines. The solid lines below THz indicate fits with the sum of dc conductivity and the UDR. The dash-dotted lines demonstrate a slope of one; the dashed lines indicate the SLPL. The inset shows the high-frequency dielectric loss minimum of CdF_2:In; the dashed lines are guides for the eyes.
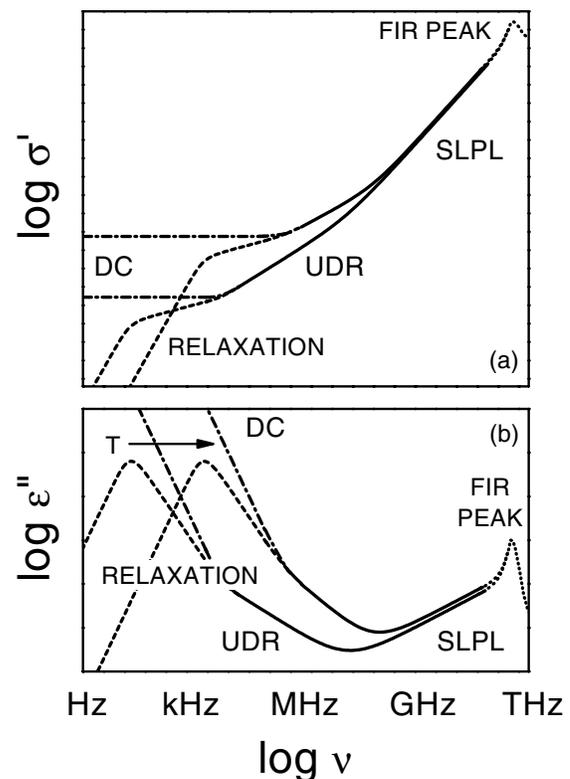

FIG. 4. Schematic view of the frequency-dependent response of disordered matter for two temperatures. At low frequencies for nonconducting dipolar systems, relaxational behavior is observed (dashed lines; the case of a system with an excess wing is shown), which is replaced by dc conductivity for the conducting systems (dash-dotted lines). The region of universality is indicated by the solid lines. In the far-infrared (FIR) region, microscopic excitations (phonon resonances or boson peak, dotted line) show up. At the abscissa, a rough indication of the frequency ranges is given.

increase of ε'' (corresponding to $\sigma' \sim \nu^2$). Clearly, there must be an additional contribution—the SLPL. Only in PC at the lowest temperature, the experimental data are nearly matched by this ansatz. However, one has to be aware that an $\varepsilon'' \sim \nu$ increase corresponds to a Debye relaxational behavior, and it is likely that the actual increase towards the boson peak is steeper. In literature, a number of explanations for a SLPL can be found: For supercooled liquids, the mode-coupling theory (MCT) predicts a shallow high-frequency minimum in $\varepsilon''(\nu)$ with a high-frequency flank following a power-law ν^a, with $a < 0.4$ [25]. A different explanation was proposed in terms of a nearly constant loss contribution [comprising also a superlinear $\sigma'(\nu)$ with $1.2 < n < 1.3$], ascribed to a vibrational relaxation process [26]. Finally, some theories on hopping conduction may also allow for a superlinear behavior in certain cases [21,27]. It should be noted that the observed SLPL most likely is not connected to the photon-assisted hopping, recently observed in various semiconductors at low temperatures and high frequencies [14]. A transition from phonon- to photon-assisted hopping should occur for $h\nu > k_B T$. However, even for temperatures as low as 5 K, this condition would be fulfilled only for $\nu > 10^{11}$ Hz, while the low-frequency onset of the SLPL in the present work varies between 10^3 (PCSMO) and 10^9 Hz (PC). Overall, none of the above explanations for SLPL can account for its occurrence in all the different types of materials reported here. In view of the similarity of the ac response of doped semiconductors to that of canonical glass formers, it seems relevant to further investigate glassy behavior of electrons. Recently, it has been shown that glassy behavior of electrons emerges before the charge carriers localize, and, in addition, that Anderson localization enhances the stability of the glass phase, while Mott localization tends to suppress it [28]. It certainly would be an attractive idea to apply concepts, successfully used for canonical glass formers (as, e.g., the MCT), to disordered electronic systems. However, because these theories consider mainly density-density correlations, further theoretical work seems necessary.

In conclusion, by measuring the extreme broadband dielectric response of different disordered materials, we found an astonishing universality extending over a broad dynamic range up to the IR regime. Jonscher's UDR, characterized by a sublinear power law at intermediate frequencies, is followed by a SLPL with an exponent significantly smaller than 2. This universality is valid for liquids, supercooled liquids, glasses, ionic melts, glassy and crystalline ionic conductors, orientationally disordered crystals, and doped semiconductors, with the electromagnetic field acting on diffusing or reorienting dipoles, hopping ions, and localized holes or electrons. Thus, disordered condensed matter seems to exhibit a universal response to ac electrical fields that is far more general than thought until now. We feel that this common behavior is too striking to be accidental and believe that

one underlying principle governs the response of disordered matter to electromagnetic fields.

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