

$1/f$ noise and dynamical heterogeneity in glasses

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We investigate the relationship between two experimental sets of data related to dynamical heterogeneity, the coefficient α of $1/f^\alpha$ dipolar noise derived from the nonexponentiality of the dielectric or magnetic response near and above the mean relaxation time, and the range Δz of the relaxation times. We find that in different classes of glasses, including spin and proton glasses, relaxor materials, and glass-forming liquids, this relationship exhibits the same trend.

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Although a broad range of relaxation times is present in glasses and in several systems where $1/f$ noise is detected, the study of noise in glasses seems to have been limited to a few cases only. Actually the first question to ask is the possible occurrence of a general relationship between noise measured in a narrow region close to the mean relaxation time and the range of the full spectrum of relaxation times. This is because heterogeneity implies that the autocorrelation functions for different microscopic regions decay as simple exponentials but with different values of relaxation time, the average of these local relaxations yielding the observed stretched exponential behavior of the bulk.

In order to approach these questions from the experimental side, we shall consider below three classes (proton and magnetic spin glasses, relaxors, and glass-forming liquids) that have been widely studied by the same method, by detecting the electric or magnetic susceptibility at different temperatures T around the glass temperature T_g or the Vogel-Fulcher freezing temperature T_0 [1]. Our aim will be a comparison of the narrow range heterogeneity, as derived from the nonexponentiality of the response near and above the mean relaxation time displayed by the imaginary part of susceptibility and conveniently expressed by the coefficient α of $1/f^\alpha$ noise, with the wide range heterogeneity, as expressed by the range Δz of the observed relaxation times. This comparison will be made for each glass sample, and different classes of glasses will be later shown in the α versus Δz plane, to display a significant unity in the behavior of all collected data. To this end we shall first review briefly the experimental situation in each of these classes of glass as follows.

(i) In magnetic spin glasses a random spatial distribution of local spins together with the frustration effects associated with the competing ferro- and antiferromagnetic interactions lead to the absence of long-range magnetic order at low temperatures [2]. The real part of the complex magnetic suscep-

tibility exhibits the cusplike maximum at freezing temperature T_f , while the imaginary part shows a distinct anomaly around T_f due to the very broad distribution of relaxation times. The dynamic response has been studied in many compounds, but particularly extensively in the solid solutions $\text{Eu}_x\text{Sr}_{1-x}\text{S}$ [3,4]. Proton glasses are the dielectric equivalent of magnetic spin glasses, since, in analogy with real spin glasses, they can be defined as systems where splitting occurs between the zero-field-cooled dielectric susceptibility ε_{ZFC} and the field-cooled dielectric susceptibility ε_{FC} in the vicinity of the temperature T_g [5]. The in-phase dielectric susceptibility $\varepsilon'(\omega) = \text{Re}[\varepsilon^*(\omega)]$, where $\omega = 2\pi f$, follows a roughly paraelectric temperature dependence above the temperature T_g . Both the in-phase and out-of-phase dielectric susceptibility $\varepsilon''(\omega) = \text{Im}[\varepsilon^*(\omega)]$ show a broad dispersion on approaching T_g from above. In particular, $\varepsilon''(\omega)$ is close to zero far above T_g ; however, it starts to rise to a broad peak at some temperature above T_g at which the relaxation times exceed the experimental time scale $t_{exp} \propto 1/\omega$, thus displaying a broad range of relaxation times [6]. Freezing dynamics and the properties of the relaxation spectrum in several proton and deuteron glasses have been studied by the sensitive method of the frequency-temperature plot [7], particularly lysozyme hydrated powders [8] and mixtures of ferro- and antiferroelectric compounds such as deuterated rubidium ammonium dihydrogen phosphate (abbreviated as DRADP) [7,9] and deuterated betain phosphate betain phosphite (D-BP:BPI) [10].

(ii) A second class of materials exhibiting a glasslike freezing transition that we shall consider below is provided by relaxors. The freezing dynamics in some of these systems, such as lanthanum-modified lead zirconate titanate ceramics $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3$ (abbreviated as PLZT) and lead magnesium niobate (PMN) single crystals, which are believed to be frustrated like proton and spin glasses [11], have also been studied by the frequency-temperature plot [12,13]. The validity of the fluctuation-dissipation theorem has been proved for spin glasses [14], even in the temperature region

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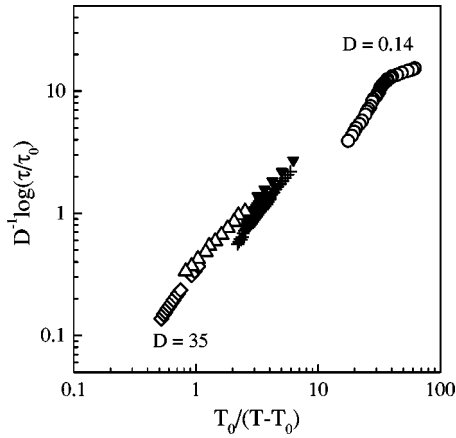


FIG. 1. Modified Angell plot for various glass-forming systems: lysozyme (\circ), $\text{Eu}_{0.40}\text{Sr}_{0.60}\text{S}$ (solid ∇), PMN crystal ($+$), 9/65/35 PLZT ceramics (\square), glycerol (\triangle), and DRADP $x=0.65$ (\diamond). The values of D are, top to bottom, lysozyme $D=0.14$, $\text{Eu}_{0.40}\text{Sr}_{0.60}\text{S}$ $D=2.9$, PMN crystal $D=4.3$, 9/65/35 PLZT ceramics $D=6.8$, glycerol $D=17$, and DRADP $x=0.65$ $D=35$.

$T < T_g$. This suggested that we also include studies of the relaxation spectrum behavior in relaxor materials below the freezing temperature.

(iii) The third class of glasses to be considered is that of structural glasses, particularly glass-forming liquids such as glycerol and *m*-fluoroaniline, since here the dielectric data are available in a wide frequency range [15–17]. These systems are well known and their heterogeneity is well understood [18], and a theory correlating the temperature variation of the stretching exponential β with the fragility has been proposed [19].

A quasistatic way to compare these materials is to evaluate the fragility D defined as the exponent in the Vogel-Fulcher divergent behavior for the viscosity $\eta \propto \exp[DT_0/(T-T_0)]$ [20]. Figure 1 shows from the viewpoint of our approach the most complete and self-consistent data for the above mentioned classes of glass-forming materials plotted in a modified Angell plot where instead of static stress we consider variable electric or magnetic stresses. Here, the divergent longest relaxation time τ [8,12,9,13] in units of the corresponding attempt frequency τ_0 is rescaled by the fragility D and plotted versus the inverse reduced temperature $T_0/(T-T_0)$. In such a representation a correlated pattern is observed in which different classes of glasses with different fragility D fall on one curve in a log-log plot with a tendency to gravitate toward larger values as the fragility D decreases. It is interesting to note that, while relaxors and glass-forming liquids overlap in the intermediate range, both fragile ($D \ll 1$, see lysozyme data) and strong ($D \gg 1$, see DRADP data) glass formers can be found within the same class of proton glasses.

Now we turn to the quantification of dynamical heterogeneity. We start by considering the narrow range heterogeneity, as exhibited by the nonexponentiality of the mean relaxation time, and typically measured by the width β of the KWW stretched exponential. It has been shown that the coefficient α of the $1/f^\alpha$ noise exhibited by the spontaneous

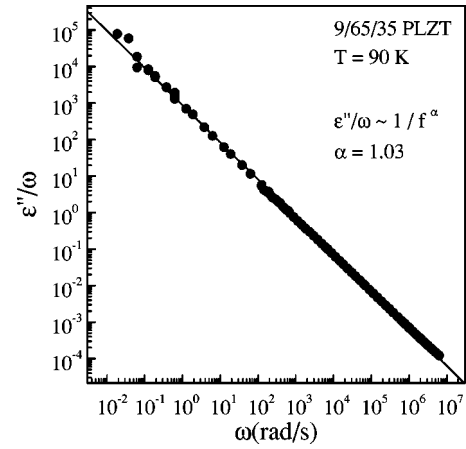


FIG. 2. Measured values of $\epsilon''(\omega)/\omega$ plotted vs ω in a log-log plot for the relaxor system 9/65/35 PLZT ceramics.

fluctuating spin or dipole moment $x(t)$ can be derived by the fluctuation-dissipation theorem $\bar{x}_\omega^2 = (\epsilon''(\omega)/(kT/\pi))$ from the slope of the spectrum $S(\omega) = \epsilon''(\omega)$ plotted versus $\omega = 2\pi f$, when $\epsilon''(\omega) \sim 1/f^\alpha$ for ω near and above the characteristic relaxation frequency f_p at which $\epsilon''(\omega)$ exhibits a peak value. Since in the case of stretched exponential relaxation the reduced width $w = W/W_D$ of the $\epsilon''(\omega)$ peak centered at f_p is approximately equal to $1/\beta$, where W is the measured full width at half maximum (FWHM) of the $\epsilon''(\omega)$ peak and W_D is the FWHM of the $\epsilon''(\omega)$ peak for Debye monodisperse relaxation, and β is the exponent of the stretched exponential response function $\phi(t) = \exp(-t/\tau)^\beta$, the experimental value of $\alpha = 1 + \beta$ can easily be evaluated from current dielectric studies. This approach has been followed recently in hydrated lysozyme powders [21], but it must be noted that the exponent α evaluated in this way is the coefficient of $1/f^\alpha$ noise only in a small frequency region close to and above the f_p defined above, and as such corresponds to the narrow range heterogeneity. In the following, special attention was always paid to this condition for all samples considered. In one case only, shown in Fig. 2, where ϵ''/ω is plotted versus ω for PLZT ceramics of composition $x = 0.09$, $y = 0.65$ (labeled as 9/65/35 PLZT) at 90 K, only the high frequency part of $\epsilon''(\omega)$ could be measured within the accessible experimental frequency window, due to the rapid slowing down of the freezing glassy dynamics [13]. For this particular instance, the slope $\alpha = 1.03$ demonstrates the occurrence of $1/f$ dielectric noise in the nonergodic relaxor phase similar to the reported $1/f$ noise in the nonergodic glassy phase of magnetic and organic glass formers [22,23].

Concerning the long-range heterogeneity, following the method of the frequency-temperature plot (a detailed description of this method was already given in Refs. [7,9]) the natural assumption is made that the distribution of relaxation times is limited by an upper cutoff z_2 and a lower cutoff z_1 [7]. Here $z_i = \ln(\omega_a \tau_i)$ with ω_a as an arbitrary frequency unit; thus a suitable measure for the total width of the relaxation spectrum $\Delta z = z_2 - z_1$ can be defined. In order to determine Δz one must apparently obtain information about the temperature variations of the relaxation spectrum, i.e., the tem-

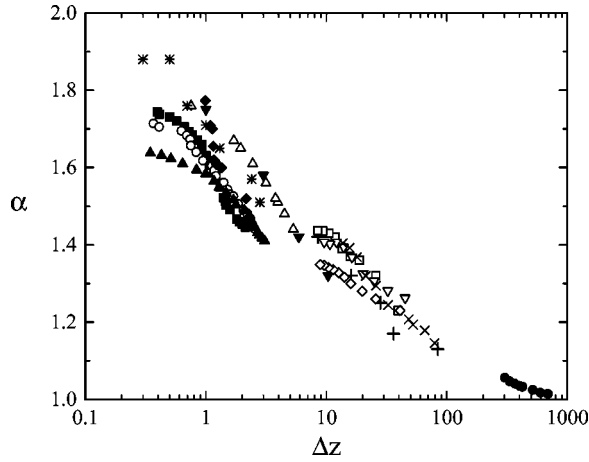


FIG. 3. α_{HF} as a function of the width of the relaxation spectrum Δz determined in various glass formers: *m*-fluoroaniline (*), glycerol (solid \diamond), lysozyme pH=7 $h=0.28$ (solid \square), lysozyme pH=7 $h=0.30$ (\circ), lysozyme pH=3 $h=0.28$ (solid \triangle), $\text{Eu}_{0.55}\text{Sr}_{0.45}\text{S}$ (Δ), $\text{Eu}_{0.40}\text{Sr}_{0.60}\text{S}$ (solid ∇), DRADP $x=0.50$ (\square), DRADP $x=0.60$ (∇), DRADP $x=0.24$ (\times), DRADP $x=0.65$ (\diamond), D-BP:BPI (40:60) (+), 9/65/35 PLZT (\bullet). Note that as $\Delta z \rightarrow \infty$ the exponent $\alpha \rightarrow 1$, i.e., $S(\omega) \rightarrow 1/f$.

perature dependences of the relaxation spectrum cutoffs z_1 and z_2 . The temperature variation of the relaxation spectrum can be directly extracted by scanning the reduced dielectric constant δ

$$\delta = \frac{\varepsilon'(\omega, T) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_{z_1}^{z_2} \frac{g(z) dz}{1 + (\omega/\omega_a)^2 \exp(2z)} \quad (1)$$

between the values 1 and 0. Here, the filter $1/[1 + (\omega/\omega_a)^2 \exp(2z)]$ in the second part of Eq. (1) is scanning the distribution of relaxation times $g(z)$ by shifting its position in ω space [7], thus probing various segments of the relaxation spectrum. The temperature dependence of the two limiting relaxation times z_1 and z_2 is then obtained in practice by finding, within the set of dielectric data at a given temperature T , a frequency $\omega = 2\pi f$ at which the prescribed value of $\delta \rightarrow 0$ and $\delta \rightarrow 1$, respectively, is reached. The total width of the relaxation spectrum is then calculated as $\Delta z = z_2 - z_1$.

Figure 3 shows the noise coefficient α as a function of the width of the relaxation spectrum Δz for all glasses mentioned above. The choice of the α versus Δz plot is convenient because, in principle, in this plot data should be contained between the two significant asymptotic values ($\alpha = 2$, $\Delta z = -\infty$), the monodispersive Debye relaxation, and

($\alpha = 0$, $\Delta z = +\infty$) the white noise at IR frequencies. Besides the intuitive meaning of the $(\alpha, \Delta z)$ plane, this might be useful in describing the behavior of other systems where α and Δz can be measured in different and appropriate ways. Here we note that data from different classes of glass do collapse toward one single curve which extends asymptotically between the Debye monodispersive relaxation ($\alpha = 2$, $\Delta z = -\infty$) and the $1/f$ noise ($\alpha = 1$, $\Delta z = +\infty$), thus covering only a portion of the surface limited between the above two asymptotic values. It should be stressed that the same trend is exhibited inside each particular glass sample. Since the data from one sample express the temperature dependence of the same sample, possible mesoscopic effects due to the different material dimensions of different samples can be ruled out [24]. It should also be noted that the data for magnetic spin glasses ($\text{Eu}_{0.55}\text{Sr}_{0.45}\text{S}$ and $\text{Eu}_{0.40}\text{Sr}_{0.60}\text{S}$) in Fig. 3 overlap data of both deuteron glasses and glass-forming liquids. Moreover, the same pattern is observed for both fragile and strong glass formers (cf. Fig. 1), thus indicating that the behavior plotted in Fig. 3 could be universal for a broad variety of glass-forming systems. Figure 3 indicates that α and Δz can be linked by a simple experimental relationship $\alpha = \alpha_0 - c \ln(\Delta z)$, where $\alpha_0 = 1.66 \pm 0.05$ and $c = 0.22 \pm 0.05$. It is interesting to note that in the case of materials exhibiting long-range order like, for instance, proper ferroelectrics or ferromagnetic materials, the width of their distribution of relaxation times does not exceed one order of magnitude, i.e., α typically exceeds the value of 1.6. This means that in contrast to glassy systems all ordered materials are contained in the upper left corner in our Fig. 3, i.e., $1.7 < \alpha < 2$ and $\Delta z < 1$. Different models for the Debye equations, like dilute solutions of dipolar molecules in a non-polar liquid, should be contained in the same upper left corner.

In conclusion, by looking at two different regions of the relaxation spectrum of several glasses, and comparing the dipolar noise near and above the mean relaxation time with the frequency range where relaxation is observed, we have found that the same trend is exhibited in spin and proton glasses, glass-forming liquids and relaxors. This result suggests the presence of an invariant relationship between narrow and wide time heterogeneity for several glasses near their freezing temperatures, an experimental relationship still to be understood from the theoretical side.

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