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Unique Non-Debye Relaxation Process and New Physical Insight for the Dielectric Loss

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Abstract

The dielectric response for a broad range of systems proves the existence of a remarkable features of frequency and time response which is basically incompatible with the variety of currently used time-honored (i) Cole-Cole (ii) Cole-Davidson (iii) Havriliak-Negami dielectric functions (iv) Kohlrausch-Williams-Watts stretched exponential function (v) Jonscher's universal dielectric response (vi) Ngai's coupling model and (vii) Dyre's random energy barrier model. The existing interpretations for these models/functions are: (a) distributions of relaxation times and (b) the energy criterion. Still, these empirical models and their theoretical interpretations are subject of debate in the literature and remain disjointed, and adapted to the individual materials. The purpose of paper is to present a novel concept of "Debye and fractional Debye type dipole" dielectric law of relaxation to the interpretation of the dielectric response of solids. The dielectric relaxation processes is based on Debye type dipole-dipole interaction initiated fractional Debye type dipoles in the wide range of materials, covering very diverse materials with physical processes-all of which show a remarkable features of the proposed relaxation behavior. The complex dielectric and relaxation functions, and their energy criterion in terms of the Debye and the fractional Debye dipole process provides a new physical insight for the α , β , γ , δ relaxations, excess wing and shoulder structure in the dielectric loss of glass formers, plastic crystals, drugs, polymers, etc. The model shows an excellent agreement with experimentally observed dielectric spectra of wide variety of materials.

1. Introduction

The dielectric response of most of the condensed matter system shows a remarkable degree of features in that its frequency dependence often follows deviation from classically expected Debye response, which in the time domain corresponds to exponential decay. The deviation of dielectric response from the Debye feature, in general, is referred as non-Debye relaxation (NDR) or many-body relaxation [1,2]. Their interpretation of temperature dependence is carried out using either individual or combination of time-honoured models like: (i) Cole-Cole (CC) [3-5] (ii) the Cole-Davidson (CD) [6] (iii) Havriliak-Negami (HN) [7] dielectric functions (iv) Kohlrausch-Williams-Watts (KWW) stretched exponential function [8,9] (v) Jonscher's universal dielectric response (UDR) [10-12] and (vi) Ngai's coupling model (CM) [2,13-15], (vii) Dyre's random energy barrier model [16-18]. Each function has different level of significance for the physical process of NDR and no consensus has been arrived so far. Therefore, there is a need of unique NDR function connecting time and frequency domains with generally acceptable microscopic physical process. In present work, we propose NDR model considering the intermolecular Debye type dipole-dipole interaction generated fractional Debye type dipole or non-Debye dipole in coupled form by considering energy criterion in the form of conservation of energy and moment.

The proposed concepts constitutes a "innovation" in thinking about dielectric relaxation and it moves away from the former interpretations which were depend on heavily on the concept of (a) distributions of relaxation times as used in CC, CD, HN, and KWW, (b) the energy criterion as used in Jonscher's UDR. The Debye-like processes supposed to be coexisting in CC, CD, HN, KWW models, whereas, Debye like process do not coexisting in the energy criterion based Jonscher's UDR and these models constitute a superficially plausible models. The existing distribution of relaxation time interpretation and energy criterion based models for the NDR do not stand up to critical examination and that a different approach is therefore essential. Our proposed model and new interpretation is based on the unique property of molecular level Debye type dipole and its interaction caused fractional Debye type dipole relaxation in coupled form of fractional Debye type dipole relaxation law in frequency that the ratio of the imaginary to the real parts of the complex dielectric is dependent on frequency, in sharp contrast to the Jonscher's UDR where this ratio is independent of wide range of frequency. Expressions for the complex dielectric and relaxation functions have been derived for the Debye and fractional Debye type dipole processes. Salient features of the proposed complex dielectric and relaxation functions

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are described and compared with time-honoured models. There are controversial results reported and debated in the literature on the interpretation of α , β , γ , and δ relaxations, and excess wing of dielectric loss data of liquids, glass formers, polymers, drugs, plastic crystals *etc*. The proposed model certainly provide new physical insight for the NDR and expected to answer many issues related to the interpretation of α , β , γ , and δ relaxations, and clarify physical picture for excess wing.

2. Debye and non-Debye dielectric functions

Debye's original model of dipolar dielectric response consists of a set of identical non-interacting dipoles free to rotate against some viscous resistance in fluid-like medium by thermal excitation between two preferred orientations separated by a potential barrier, a situation more likely to be found in solids. In a log(frequency) vs log(dielectric loss) plot the Debye dielectric loss is symmetric with respect to loss peak having slope +1 below the loss peak and -1 above loss peak and has full width at half maximum (FWHM) 1.144 decades. Typical Debye type features of dipolar behaviour may be found in few polymers in which the dipole may be well characterized both in type and in density. However, the dielectric response in several polymers and other different system departs strongly from Debye features.

Cole and Cole [3] (CC) suggested the empirical dielectric function to account for the deviation from Debye features as:

$$\epsilon_{CC}^{*}(\omega) = \epsilon_{\infty} + \frac{\Delta \epsilon_{CC}}{1 + (i\omega\tau_{CC})^{1-\alpha_{CC}}}$$
(1)

where $0 \le \alpha_{cc} < 1$ is a CC parameter depends on material, temperature and pressure, and τ_{cc} is the CC type relaxation time, $\Delta \varepsilon_{cc} = \varepsilon_s - \varepsilon_{\alpha'}$, CC dielectric relaxation strength, ε_s and ε_{∞} are respectively the high and low frequency limits. In a log(frequency) vs log(dielectric loss) plot the CC dielectric loss is symmetric with respect to loss peak, having slope (1- α_{cc})<1 below the loss peak and (1- α_{cc})<-1 above loss peak, and having FWHM greater than the Debye dielectric loss FWHM of 1.144 decades.

The dielectric loss data of many super-cooled monoalcohols and poly-alcohols have shown asymmetry with respect to loss peak having long tail or excess wing. Cole and Davidson [6] (CD) suggested the empirical formula having asymmetric loss in the dielectric function:

$$\epsilon_{CD}^{*}(\omega) = \epsilon_{\infty} + \frac{\Delta \varepsilon_{CD}}{(1 + i\omega \tau_{CD})^{\beta_{CD}}}$$
(2)

where $0 < \beta_{CD} \le 1$, is a CD parameters depends on material, temperature and pressure and τ_{CD} is the CD type relaxation time, $\Delta \varepsilon_{CD} = \varepsilon_s - \varepsilon_{\omega}$, CD dielectric relaxation strength, ε_s and ε_{ω} are respectively the high and low frequency limits. In a log(ω) vs log(dielectric loss) plot the CD dielectric loss is asymmetric with respect to loss peak having slope 1 below the loss peak and < -1 above loss peak.

Some super-cooled systems, polymers and plastic crystals and glasses have CC type spectra at low frequencies and CD type spectra at high frequencies. In work of Havriliak and Negami [7] proposed the following empirical form dielectric function:

$$\epsilon_{HN}^{*}(\omega) = \epsilon_{\infty} + \frac{\Delta \varepsilon_{HN}}{((1 + (i\omega\tau_{HN})^{1 - \alpha_{HN}})^{\beta_{HN}}}$$
(3)

where $0 \le \alpha_{\rm HN} < 1$ and $0 < \beta_{\rm HN} \le 1$ are parameters depends on material, temperature and pressure and $\tau_{\rm HN}$ is HN type relaxation time. In a log(frequency) vs log(dielectric loss) plot the HN dielectric loss is asymmetric with respect to loss peak having slope <1 below the loss peak and < -1 above loss peak and having FWHM greater than the Debye dielectric loss FWHM of 1.144 decades.

The inverse Laplace transform of Eqs. (1)-(3) into the time domain are *not* analytical functions. For the time dependence polarization current description KKW [8,9] empirical function:

$$i_{KWW}(t) \propto \phi_{KWW}(t) \propto \exp\left(-(t/\tau_{KWW})^{\beta_{KWW}}\right)^{(4)}$$

is used, where $0 < \beta_{KWW} \le 1$, the exponent β_{KWW} is a stretching parameter, and lower the β_{KWW} value the more stretching is the relaxation function and τ_{KWW} is the KKW relaxation time. The stretching can formally be explained by assuming a superposition of exponentials with distribution of relaxation times.

Jonscher has reviewed phenomenology of dielectric response in wide range materials. He has derived the so-called "universal dielectric response" by examining the dielectric loss in the frequency and time domains and tentatively modelled in terms partial charge screening process [10-12]. Jonscher found that the power law is a manifestation of a universal mechanism in which the energy loss per cycle to the energy stored per cycle is independent of frequency rather than being the result of superposition of Debye like loss with distribution of relaxation time as in CC, CD, HN and KWW. Jonscher's empirical form of dielectric loss is:

$$\varepsilon^{\prime\prime}(\omega) \propto [(\omega/\omega_2)^{-m} + (\omega/\omega_1)^{(1-n)}]^{-1}$$
(5)

where m and (1-n) are both smaller than unity, ω_1 , ω_2 and ω_p are thermally activated hopping parameters. In a log(frequency) vs log(dielectric loss) plot the UDR is asymmetric with respect to loss peak having slope m<1 below the loss peak and (1-n)< -1 above loss peak and having FWHM greater than the Debye dielectric loss FWHM of 1.144 decades, and normally m is greater than n. The empirical form for polarization current Eq. (5) is proposed as

$$i(t) \propto [(t\omega_{\rm p})^{1+m} + (t\omega_{\rm p})^n]^{-1}.$$
 (6)

A change in slope has been shown in double logarithmic time-domain plot with sum of two consecutive independent displacement current in the material medium. Jonscher's empirical form of dielectric function exponent's (n, m) are *not* related each other, and the exponents $\alpha_{CC'}$ $\beta_{CC'}$ ($\alpha_{HN'}$ β_{HN}) and β_{KWW} and their use in dielectric loss data interpretation is still debatable in the literature.

3. Debye and fractional Debye type dipole dielectric functions

3.1 Debye and fractional Debye type dipole process

Let the condensed matter system consist of molecules with reorientation of dipolar entities with Debye type dipole moment \mathbf{G}_0 . In an electric field under a given thermodynamic condition, the instantaneous transfer of dipole moment \mathbf{G}_0 is not possible for a given molecular process due to intermolecular Debye type dipole-dipole interactions. The fraction of Debye type dipole that has not been transferred instantaneously is defined as $\pm \mathbf{G}=(1-g_d)$ \mathbf{G}_0 , where $0 < g_d < 1$. The consequence of these interaction is the shift in the magnitude of Debye dipole moment \mathbf{G}_0 by an equal magnitude of $\pm \mathbf{G}=(1-g_d)\mathbf{G}_0$ as illustrated in Fig.1. Debye type \mathbf{G}_0 dipoles evolved with these interaction as fractional Debye type dipoles [19,20]:

$$G_{+}=G_{0}+G=(2-g_{d})G_{0'}$$
 and $G_{-}=G_{0}-G=g_{d}G_{0'}$ (7)

where N number of Debye type G_0 per unit volume and becomes N/2 pairs of $G_{\pm'}$ and dipole moment of G_{\pm} and G_{-} is increased and decreased respectively by a factor of $(1-g_d)$ with respect to G_0 . These type of dipole moment evolution in condensed matter systems lead to potential energy landscaping, a complicated dependence of energy on configuration, and a change in configurational entropy and a change in fragility, a measure of rapidity with which the liquid's properties like viscosity changes.

The average dipole moment is determined by using Langevin function for Debye type dipole and fractional Debye type dipole and it is found to be:

$$<\mu_i>=\mu_i L(z_i), L(z_i)=coth(z_i)-1/z_i$$



Fig. 1: Scheme showing Debye type dipole G_0 (black vector, $g_d=1$) and fractional Debye type dipole G_- (red vector) and G_+ (blue vector) on the left panel, $0 < g_d < 1$. Langevin functions for the Debye type dipole G_0 (black line, $g_d=1$) and fractional Debye type dipole G_- (red line) and G_+ (blue line) for $0 < g_d < 1$.

where $z_i = \mu_i E / (k_{\rm B}T)$, E is external applied electric field, the symbols <> stand for ensemble average for the dipoles and μ_i stands for the dipoles G_{μ} G_{\perp} and G_{\perp} . The statistical distribution of irreversible processes follows the Boltzmann factor $exp[-(U_i/k_pT)], U_i=G_icos(\theta_i)E$, where the energy of $G_{0'}$ is redistributed through, G_{-} , and G_{+} , such that total energy is conserved, and θ_i is angle between dipole moment and E. In Fig.1, in the right panel, for $z_i >>1$ the $L(z_i)=1-1/z_i$ and approaches to one, however, for low field limit $z_i <<1$, the linear regime $L(z_i) = (1/3)z_i$ and saturation *depends* on fractional Debye type dipole strength g_{d} . The energy and moment of the dipole G_{-} and \mathbf{G}_{\perp} is shifted with respect to \mathbf{G}_{α} in equal magnitude, and the total energy and moment of the system is conserved. Since, the energy of Debye dipole G_0 is redistributed through the fractional Debye type dipole pair $G_{+'}$ the dielectric loss spectra of G_{+} spreads with respect Debye type dipole \mathbf{G}_0 dielectric loss spectra.

3.2 Dielectric and relaxation functions for Debye type dipole G_0

Debye type dipole dielectric function provides unique information pertaining to the molecular process of matter, structure, chemical composition. The Debye relaxation function and Debye dielectric function for the non-interacting Debye type dipole \mathbf{G}_0 is the earliest known functions for the description of dielectric relaxation process and it can be obtained Laplace transform of negative derivative of dielectric relaxation function and it is found to be:

$$[i_d(t)]_{\boldsymbol{G}_0} \propto [\boldsymbol{\phi}_d(t)]_{\boldsymbol{G}_0} \propto exp\left[-\left(\frac{t}{\tau_D}\right)\right] \propto exp\left[-\left(\frac{T}{\Gamma}\right)_{\boldsymbol{G}_0}\right]$$

ith $(T)_{\boldsymbol{G}_0} = t$, $(\Gamma)_{\boldsymbol{G}_0} = \tau_d = \tau_D$, for $g_d = 1$ (9a)

W

(8)

$$[\epsilon_d^*(\omega)]_{\boldsymbol{G}_0} - \epsilon_{\infty} = \frac{(\Delta\epsilon)_{\boldsymbol{G}_0}}{(1+i\omega\tau_D)} = \left(\frac{\Delta\epsilon}{1+S\Gamma}\right)_{\boldsymbol{G}_0}, (S)_{\boldsymbol{G}_0} = i\omega,$$

(Γ)_{\boldsymbol{G}_0} = $\tau_D, g_d = 1,$ (9b)

$$(\Delta \epsilon)_{\boldsymbol{G}_0} = (\epsilon_s - \epsilon_\infty)_{\boldsymbol{G}_0} = N \frac{G_0^2}{3\epsilon_0 k_B T} - \epsilon_\infty, \tag{9c}$$

where $[\phi_a(t)]_{G_0}$ and $[\epsilon_a^*(\omega)]_{G_0}$ is the dielectric relaxation and complex dielectric functions for the Debye type dipole moment \mathbf{G}_0 , τ_D is the Debye dielectric relaxation time, $\mathbf{s}=i\omega$ is Laplace transform parameter, ω is the frequency of an external applied electric field, *i* is the complex unit accounts for the energy loss mechanism in frequency domain, $(\Delta \epsilon)_{G_0}$ the dielectric strength for Debye mechanism, N is the density of dipoles, T is the temperature, ε_s and ε_{∞} are respectively the high and low frequency limits. The normalized Debye function Eq. (9a) has dielectric loss peak $\omega \tau_D = \tan(\pi/4) = 1$, which is symmetric on a log-log plot having slope 1 on the left side and -1 on the right side of loss peak respectively and has full width at half maximum (FWHM) of 1.144 decades [10].

3.3 Dielectric and relaxation functions for the fractional Debye type dipole G_

The complex dielectric function for the fractional Debye type dipole $G_{-}=g_{d}G_{0}$ is obtained by incorporating the consequence of $-\mathbf{G}=(1-g_d)\mathbf{G}_0$ on $\mathbf{G}_{0'}$ where $[\boldsymbol{\epsilon}_{\mathbf{d}}^*(\boldsymbol{\omega})]_{\mathbf{G}_0}$ is the Debye type dipole complex dielectric function. The consequence of -G on the Debye type dielectric function and complex dielectric function is shifting of the Debye type dipole relaxation term t/τ_d , and $i\omega\tau_d$ by a factor of $(t/\tau_d)^{1-g_d}$, $(i\omega\tau_d)^{1-g_d}$ and hence the Debye type dipole terms t/τ_d and $i\omega\tau_d$ become fractional Debye type dipole relaxation terms in the time domain as $(t/\tau_d)/(t/\tau_d)^{1-g_d} = (t/\tau_d)^{g_d}$ in the frequency domain as $i\omega \tau_d/(i\omega \tau_d)^{1-g_d} = (i\omega \tau_d)^{g_d}$. In terms of dipole energy, the Debye type dipole energy is decreased by a factor of $(1-g_d)$. The dielectric relaxation and complex dielectric functions are obtained for the fractional Debye type dipole $G_{=}g_{d}G_{0}$ by changing the Laplace transform variables $\mathbf{t} = (\mathbf{T})_{G_0}$ and $\mathbf{\tau}_d = (\mathbf{\Gamma})_{G_0}$, $(\mathbf{s})_{G_0} = i\boldsymbol{\omega}$ as $t^{g_d} = (T)_G, \quad \tau_d^{g_d} = (\Gamma)_G, \ (s)_{G_-} = (s)_{G_0}/(s^{1-g_d})_{G_0}$ $[i_d(t)]_{\boldsymbol{G}_-} \propto [\phi_d(t)]_{\boldsymbol{G}_-} \propto exp\left[-\left(\frac{t}{\tau_d}\right)^{g_d}\right] \propto exp\left[-\left(\frac{T}{\Gamma}\right)_{\boldsymbol{G}_-}\right],$ $[\epsilon_d^*(\omega)]_{\boldsymbol{G}_-} - \epsilon_{\infty} = \frac{(\Delta\epsilon)_{\boldsymbol{G}_-}}{1 + (i\omega\tau_d)^{\boldsymbol{g}_d}} = \left(\frac{\Delta\epsilon}{1+S\Gamma}\right)_{\boldsymbol{G}_-}, (S)_{\boldsymbol{G}_-} = \frac{s}{s^{1-\boldsymbol{g}_d}}, {}^{1}\right)$

$$(\Gamma)_{\mathbf{G}_{-}} = \tau_d^{g_d}, \ s = i\omega, \tag{10b}$$

where

$$(\Delta \epsilon)_{\boldsymbol{G}} = (\epsilon_{s} - \epsilon_{\infty})_{\boldsymbol{G}} = \frac{N}{2} \frac{G^{2}}{3\epsilon_{0}k_{B}T} - \epsilon_{\infty}, \qquad (10c)$$

is the dielectric strength of G_{-} which is differ from Debye type dielectric strength, ϵ_s and ϵ_∞ are the high and low external frequency dielectric limits respectively, N is G_{-} dipole density. This is similar to CC type complex dielectric function [3], however, $(\Delta \epsilon)_{\mathbf{G}}$ is different from $(\Delta \epsilon)_{\mathbf{G}_0}$ since number density N and average dipole strength are altered by the manifestation of 'many-particle' like intermolecular interaction mechanism. The fractional Debye type dipole strength indicate strength of interaction in terms of exponent when $0 < g_d < 1$, and for the Debye type dipole process, $g_d = 1$ and it is a manifestation of 'single-particle' like molecular interaction mechanism.

3.4 Dielectric and relaxation functions for the fractional Debye type dipole G₊.

The complex dielectric function for fractional Debye type dipole $G_{+}=g_dG_0$ is obtained by incorporating the

consequence of $+G=(1-g_d)G_0$ on $G_{0'}$ where $[\epsilon_d^*(\omega)]_{G_0}$ is the Debye type dipole complex dielectric function. The consequence of G on the Debye type dielectric function and complex dielectric function is shifting of the Debye type dipole relaxation term t/τ_d and $i\omega\tau_d$ by a factor of $(t/\tau_d)^{-(1-g_d)}$, $((-i)\omega\tau_d)^{-(1-g_d)}$ and hence the Debye type dipole terms, t/τ_d and $i\omega\tau_d$ become fractional Debye type dipole relaxation terms in the time domain as $(t/\tau_d)/(t/\tau_d)^{-(1-g_d)} = (t/\tau_d)^{2-g_d}$, in the frequency domain as $i\omega\tau_d/((-i)\omega\tau_d)^{-(1-g_d)} = i^{g_d}(\omega\tau_d)^{2-g_d}$. In terms of dipole energy, the Debye type dipole energy is *increased* by a factor of $(1-g_d)$. The dielectric relaxation and complex dielectric functions are obtained for the fractional Debye type dipole $G_+=(2-g_d)G_0$ by changing the Laplace transform variables $t = (T)_{G_0}$ and $\tau_d = (\Gamma)_{G_0}$

$$(\mathbf{s})_{G_0} = i\boldsymbol{\omega} \quad \text{as} \ \mathbf{t}^{2-g_d} = (\mathbf{T})_{G_+},$$

$$\mathbf{\tau}_d^{2-g_d} = (\mathbf{\Gamma})_{G_+}, \ (\mathbf{s})_{G_+} = (\mathbf{s})_{G_0} / ((-\mathbf{s})^{-(1-g_d)})_{G_0},$$

$$[i_d(t)]_{G_+} \propto [\phi_d(t)]_{G_+} \propto exp\left[-\left(\frac{t}{\tau_d}\right)^{2-g_d}\right] \propto exp\left[-\left(\frac{T}{\Gamma}\right)_{G_+}\right],$$

$$(T)_{G_+} = t^{2-g_d}, \ (\Gamma)_{G_-} = \tau_d^{2-g_d}, \ 0 < g_d < 1,$$
(11b)

$$[\epsilon_d^*(\omega)]_{\boldsymbol{G}_+} = \frac{(\Delta\epsilon)_{\boldsymbol{G}_+}}{1+i^{g_d}(\omega\tau_d)^{2-g_d}} = \left(\frac{\Delta\epsilon}{1+S\Gamma}\right)_{\boldsymbol{G}_+},$$

$$(s)_{\mathbf{G}_{+}} = \frac{(s)_{\mathbf{G}_{0}}}{((-s)^{-(1-g_{d})})_{\mathbf{G}_{0}}}, (\Gamma)_{\mathbf{G}_{+}} = \tau_{d}^{g_{d}}, \ s = i\omega, (11b)$$

where

$$(\Delta \epsilon)_{\boldsymbol{G}_{+}} = (\epsilon_{s} - \epsilon_{\infty})_{\boldsymbol{G}_{+}} = \frac{N}{2} \frac{G_{+}^{2}}{3\epsilon_{0}k_{B}T} - \epsilon_{\infty}, \qquad (11c)$$

is the dielectric strength of G_+ which is differ from dielectric strength of G_- , ϵ_s and ϵ_∞ are the high and low external frequency permittivity limits respectively, N is G_+ dipole density. Equation (11b) is completely different from CC type complex dielectric function and it is second consecutive secondary fractional Debye type dipole process dielectric function related to Debye type dipole dielectric relaxation process. The $(\Delta \epsilon)_{G_+}$ is different from , since number density N and average dipole strength are altered by the manifestation of 'many-particle' intermolecular interaction mechanism. The fractional Debye type dipole strength indicate strength of interaction in terms of exponent $0 < g_d < 1$.

3.5 Unique non-Debye relaxation and the energy criterion

We have shown unique NDR process in Eqs. (9)-(11) both in frequency-time domains consists of (a) primary Debye type dipole process dielectric response and and (b) two consecutive secondary fractional Debye type dipole processes dielectric response and , and and containing the primary process in both the consecutive secondary processes, where total energy loss of Debye type dipole process and total Debye type dipole moments are conserved. Energy criterion for proposed model is shown in terms energy loss and energy storage of G_0 , G_- , and G_+ . For the dipole density N of Debye type dipoles G_0 (absence of dipole-dipole interactions) the energy criterion is given by classical case of Debye dielectric response, and the ratio of energy loss and energy storage is obtained by Eq. (9a) as:

$$\left(\frac{\epsilon_d''(\omega)}{\epsilon_d'(\omega)}\right)_{\boldsymbol{G}_0} = -(\omega\tau_D)_{\boldsymbol{G}_0}, \text{ at } \omega = 1/\tau_D, \ (\omega\tau_D)_{\boldsymbol{G}_0} = \tan(\pi/4) = 1, \ g_d = 1,$$
(12)

where the real and imaginary parts of $[\epsilon_{a}^{*}(\omega)]_{\boldsymbol{G}_{0}}$ are,

$$(\epsilon_d'(\omega) - i\epsilon_d''(\omega))_{\boldsymbol{G}_0} \propto \left(\frac{1}{1 + (\omega\tau_D)^2} - i\frac{\omega\tau_D}{1 + (\omega\tau_D)^2}\right)$$
(13)

As explained earlier, Debye type dipole-dipole molecular interaction and their evolution transform the N dipoles into N/2 dipoles of G_{-} and N/2 dipoles of G_{+} by distributing the Debye type dipole energy and moment, where the total Debye type dipole moment and energy is conserved in the processes. For the fractional type Debye type dipoles G_{-} , the energy criterion is similar to the classical case of Debye dielectric response result with a dispersion different from classical case of Debye dielectric response and the ratio of energy loss and energy storage is obtained by using Eq. (10b) as:

$$\begin{pmatrix} \frac{\epsilon_d''(\omega)}{\epsilon_d'(\omega)} \end{pmatrix}_{\boldsymbol{G}_-} = -\frac{(\omega\tau_d)^{g_d} \sin\left(\frac{g_d\pi}{2}\right)}{\left(1 + (\omega\tau_d)^{g_d} \cos\left(\frac{g_d\pi}{2}\right)\right)}, \text{ at } \omega = 1/\tau_d,$$

$$\frac{(\omega\tau_d)^{g_d} \sin\left(\frac{g_d\pi}{2}\right)}{\left(1 + (\omega\tau_d)^{g_d} \cos\left(\frac{g_d\pi}{2}\right)\right)} = \tan\left(\frac{g_d\pi}{4}\right), 0 < g_d < 1,$$

$$(14)$$

where the real and imaginary parts of $[\epsilon_d^*(\omega)]_G$ are,

$$(\epsilon_d'(\omega) - i\epsilon_d''(\omega))_{\boldsymbol{G}_-} \propto \left(\frac{1 + (\omega\tau_d)^{g_d} \cos\left(\frac{g_d\pi}{2}\right)}{1 + 2(\omega\tau_d)^{g_d} \cos\left(\frac{g_d\pi}{2}\right) + (\omega\tau_d)^{2g_d}} - i\frac{(\omega\tau_d)^{g_d} \sin\left(\frac{g_d\pi}{2}\right)}{1 + 2(\omega\tau_d)^{g_d} \cos\left(\frac{g_d\pi}{2}\right) + (\omega\tau_d)^{2g_d}} \right)$$
(15)

For the fractional type Debye type dipoles G_{+} , the energy criterion is again similar to the classical case of Debye dielectric response result with a dispersion different from classical case of Debye dielectric response and the ratio of energy loss and energy storage is obtained by using Eq. (11b) as:

$$\begin{pmatrix} \epsilon_d''(\omega) \\ \epsilon_d'(\omega) \end{pmatrix}_{\boldsymbol{G}_+} = -\frac{(\omega\tau_d)^{2-g_d} \sin\left(\frac{g_d\pi}{2}\right)}{\left(1+(\omega\tau_d)^{2-g_d} \cos\left(\frac{g_d\pi}{2}\right)\right)}, \text{ at } \omega = 1/\tau_d,$$

$$\frac{(\omega\tau_d)^{2-g_d} \sin\left(\frac{g_d\pi}{2}\right)}{\left(1+(\omega\tau_d)^{2-g_d} \cos\left(\frac{g_d\pi}{2}\right)\right)} = \tan\left(\frac{g_d\pi}{4}\right), 0 < g_d < 1,$$

$$(16)$$

where the real and imaginary parts of $[\epsilon_d^*(\omega)]_{G_+}$ are ,

$$(\epsilon'_{d}(\omega) - i\epsilon''_{d}(\omega))_{\mathbf{G}_{+}} \propto \left(\frac{1 + (\omega\tau_{d})^{2-g_{d}} \cos(\frac{g_{d}\pi}{2})}{1 + 2(\omega\tau_{d})^{2-g_{d}} \cos(\frac{g_{d}\pi}{2}) + (\omega\tau_{d})^{2(2-g_{d})}} - i\frac{(\omega\tau_{d})^{2-g_{d}} \sin(\frac{g_{d}\pi}{2})}{1 + 2(\omega\tau_{d})^{2-g_{d}} \cos(\frac{g_{d}\pi}{2}) + (\omega\tau_{d})^{2(2-g_{d})}} \right)$$

$$(17)$$

The proposed model is a coupled form Debye type dipole and fractional Debye type dipole processes and the primary relaxation time is Debye type dipole relaxation time and it is designated as $\tau_{D'}$ where the exponent g_d =1, and when 0<g_d<1, the relaxation time is designated as $\tau_{d'}$.



Fig. 2: Polarization relaxation function for the Debye type dipole G_0 polarization (dashed black line) and fractional Debye type dipole G_- (red small dotted line $g_d=0.6$), G_+ (blue bigger dotted line, $g_d=0.4$) and G_-+G_+ (green thick line $g_d=0.4$, thin line $g_d=0.6$) polarization (left panel). The red arrow indicates Debye relaxation time (1s), and the red dots indicate slow relaxation time τ_s^* and blue dots indicate fast relaxation time τ_f^* for $g_d=0.6$, 0.4 respectively. These time scales are defined as NDR times due to the fractional Debye type dipole processes and it is dynamically correlated to the Debye type dipole relaxation time τ_D . The right panel shows NDR times τ_s^* and τ_f^* as function interaction strength g_d based on Eqs. (18) & (19).

3.6 Slow and fast relaxation times in the fractional Debye type dipole process

According to the proposed model both Debye type and fractional Debye dipole processes have relaxation time $\tau_D = \tau_d$ and it is a primary relaxation time. Then, what is the relaxation time for the fractional Debye type dipole process? A careful analysis of Debye type dipole and the fractional Debye type dipole energy criterion provided two relaxation time scales correlated to primary relaxation time τ_D . By equating Debye type dipole process dielectric loss energy to fractional Debye type dipole process dielectric loss energy,

$$[\epsilon_d''(\omega)]_{\boldsymbol{G}_0} = [\epsilon_d''(\omega)]_{\boldsymbol{G}_-} \text{ or } [\epsilon_d''(\omega)]_{\boldsymbol{G}_0} = [\epsilon_d''(\omega)]_{\boldsymbol{G}_+} \text{ or } |$$
$$[\epsilon_d''(\omega)]_{\boldsymbol{G}_0} = [\epsilon_d''(\omega)]_{\boldsymbol{G}_-} + [\epsilon_d''(\omega)]_{\boldsymbol{G}_+}$$

at the loss peak $\omega = 1/\tau_d$, we obtained slow and fast relaxation time with respect to primary relaxation time τ_D respectively as:

$$\tau_s^* = 1/\omega_s^* = \tau_D(c + \sqrt{c^2 - 1}), 0 < g_d < 1, \tau_s^* = \tau_D, g_d = 1, (18)$$

$$\tau_f^* = 1/\omega_f^* = \tau_D(c - \sqrt{c^2 - 1}), 0 < g_d < 1, \tau_f^* = \tau_D, g_d = 1, (19)$$

where $c=cot(g_d\pi/4)$ is the dielectric loss of G_0 or G_- or \mathbf{G}_{+} or $\mathbf{G}_{-}+\mathbf{G}_{+}$ at the loss peak $\omega=1/\tau_{d}$. The polarization relaxation for the Debye type dipole G_0 (dashed black) and fractional Debye type dipole G_{-} (red small dots g_{d} =0.6), G_{+} (blue bigger dots, g_{d} =0.4) and $G_{-}+G_{+}$ (green thick line $g_d=0.4$, thin line $g_d=0.6$) dipoles (left panel) are shown in Fig. 2, based on Eqs. (9a)-(11a) respectively. The argument of Debye type dipole t/τ_D is shortened and lengthened by equal magnitudes above and below the Debye relaxation time in the fractional Debye type dipole representation by the exponents g_d and $(2-g_d)$. These arguments are represented as $(T/\Gamma)_{G_{-}}$ and $(T/\Gamma)_{G_{+}}$ in the fractional Debye type dipole polarization process. The shortened argument becomes $(T/\Gamma)_{G_{-}}$ stretched and lengthened argument $(T/\Gamma)_{G_+}$ becomes compressed in the Debye type exponential argument. These features are shown in Fig. 2, for g_{d} =0.6, and 0.4 as red dashed and blue dotted lines and green thick and thin lines are sum of fractional Debye type dipole polarization for g_{d} =0.6 and 0.4. Exactly similar features are observed in the frequency-domain dielectric response. The red arrow indicates Debye relaxation time (1s). The red dots indicate slow relaxation time τ_s^* and blue dots indicate fast relaxation time τ_f^* for $g_d=0.6$, and 0.4 respectively. These time scales are defined as NDR times due to the fractional Debye type dipole processes and it is dynamically correlated to the Debye type dipole relaxation time $\tau_{_D}$ The right panel shows NDR times τ_s^* and τ_f^* as function interaction strength g_d based on Eqs. (18) & (19).

The salient features of slow and fast relax on time scales are (a) the shift in Debye type relaxation time τ_D in equal magnitude on both side of Debye relaxation time (b) the magnitude of the shift in time scale depends on strength of fractional Debye type dipole in terms $0 < g_d < 1$, and smaller the magnitude g_d , stronger is the interaction strength and larger is the shifts in slow and fast relaxation times. (c) In the frequency-domain, the slow and fast relaxation times belong to left side and right side of Debye loss peak respectively for given g_d and vice-versa in the

time-domain Debye type polarization. These are *novel* result on the relaxation dynamics of the proposed model.

When the dielectric loss spectra has more than one process loss peak contributions, like, high frequency loss peak β , in addition to low frequency loss peak α , then the similar fractional Debye type contribution process is considered for the loss peak β . If the dielectric loss spectra has 'n' number fractional Debye type dipole processes and if there is loss contribution due dc conductivity $\sigma_{dc'}$ as observed in several glass forming alcohols, then the complex dielectric function and relaxation function become:

$$\epsilon_{GG}^*(\omega) = \sum_{m=1}^n ([\epsilon_d^*(\omega)]_{\mathbf{G}_-} + [\epsilon_d^*(\omega)]_{\mathbf{G}_+})_m + \sigma_{dc}/(i\omega\epsilon_0)$$
(20)

$$\phi_{GG}(t) \propto i_{GG}(t) \propto \sum_{m=1}^{n} ([\phi_d(t)]_{G_-} + [\phi_d(t)]_{G_+})_m \quad (21)$$

Here 'n' may be treated as number of subunit or subgroup or subunit of cluster of molecular level polarization processes contributing to the complex dielectric and polarization relaxation with their respective Debye type dipole and fractional Debye type dipole processes. In a nutshell, in a molecular level, for 'n' number of Debye type and their corresponding molecular level interaction initiated fractional Debye dipoles, the polarization mechanism and their dielectric function is found to be:

$$\left(\left(\frac{dP}{dT}\right)_{G_0,G_{\pm}} + \left(\frac{P}{\Gamma}\right)_{G_0,G_{\pm}}\right)_n = 0, \tag{22}$$

$$(\boldsymbol{P}(T)_{\boldsymbol{G}_0,\boldsymbol{G}_{\pm}})_n \propto \left(exp\left[-\left(\frac{T}{\Gamma}\right)_{\boldsymbol{G}_0,\boldsymbol{G}_{\pm}} \right] \right)_n$$
(23)

$$([\epsilon_d^*(\omega)]_{\boldsymbol{G}_0,\boldsymbol{G}_{\pm}})_n \propto \left(\left(\frac{\Delta \varepsilon}{1+S\Gamma} \right)_{\boldsymbol{G}_0,\boldsymbol{G}_{\pm}} \right)_n, \tag{24}$$

where 'n' represents n number of unique NDR processes having n number of temporal and spatial scales due to the n number of Debye type dipole and their respective fractional Debye type polarization relaxation processes.

The relaxation time of glass formers shows a deviation from Arrhenius law and it is parameterized with Vogel-Fulcher-Tamman (VFT) equation [21]:

$$(\tau_{d})_{n} = (\tau_{0} \exp(A_{0}T_{0}/(T-T_{0})))_{n'}$$
 for $T > T_{g'}$ (25)

where n=1, 2, ..., T_0 is the VFT approximation of the ideal glass transition temperature, A_0 is the strength

parameter, τ_0 is a pre-factor of the order inverse phonon frequency and further characterized based on fragility index [21],

$$m_{p} = log_{10}(e)(A_{0}(T_{0}/T_{g})(1 - T_{0}/T_{g})^{-2})_{n'}$$
(26)

where Arrhenius equation is

$$(\tau_{d})_{n} = (\tau_{0} \exp(E_{a}/k_{B}T))_{n'}$$

$$(27)$$

with E_{α} is activation energy. The relaxation parameters resulting from the fits are shown and the relaxation times are checked for Arrhenius or Vogel–Fulcher–Tammann (VFT) behavior.

3.7 Comparison with existing non-Debye relaxation

In **Fig. 3**, in the left panel, the existing NDR functions KWW (numerical Fourier transform for β_{KWW} =0.6), CC, CD, HN, UDR and proposed **GG function** are shown in double logarithmic plots. The empirical form of CC dielectric function has a slope (1- α_{CC}) below the loss peak and -(1- α_{CC}) above the loss peak and loss curve is symmetric about the loss peak.



Fig. 3: In the left panel, a comparison of frequency domain double logarithm plots of proposed unique NDR function (n=1) with existing NDR functions KWW (numerical Fourier transform for $\beta_{KWW}=0.6$), CC, CD, HN, and UDR. The slope of lines to which peaks is asymptotic. Plots are vertically separated by 1.5 units for clarity. The dashed line is Debye type dielectric loss. The right panel shows further details of proposed dielectric loss contribution for Debye type dipole G_0 and the fractional Debye type dipoles G_{-} , G_{+} and their sum $G_{-}+G_{+}$. The slopes varies from g_d to $2-g_d$ on left side of the loss peak and $-g_d$ to $-(2-g_d)$ on right side of the loss peak The red and blue dots on the lines show the slow and fast relaxation times for $g_d=0.4$.

The fractional exponent $(1-\alpha_{cc})$ is explained in terms equivalent circuit with impedance polarization "denoting the storage of energy in addition to dissipation energy in the mechanism of molecular interaction responsible for dispersion". The empirical function CD accounts for asymmetry in the dielectric loss observed several glass forming alcohols, however, the exponent β_{CD} is physically

uninterpreted quantity and slope of the dielectric loss below the loss peak is always one and above loss peak is $-\beta_{CD}$. The HN dielectric function was suggested when the slopes are different on both sides of dielectric loss peak, HN exponents (1- $\alpha_{_{HN}}$) and $\beta_{_{HN}}$ are physically uninterpreted quantities. However, the exponents of KWW, CC, CD and HN are used to describe distribution relaxation in NDR process. In Jonscher's UDR, the exponents 0<m<1 and 0<n<1 change the slopes of the dielectric loss curve asymmetrically with respect to loss peak having sum of two processes with exponents m and n. The energy criterion has been given for process involving only the exponent n and it is tentatively modeled in terms of partial screening mechanism. The time domain polarization functions for these existing empirical form of NDR are still a mystery, however, power laws and KWW function are approximated as possible polarization functions. It is clear from left panel of Fig. 3, the slop of proposed GG dielectric function in double logarithmic plots have completely different features when compared with existing empirical form of dielectric functions. The dielectric loss slope of sum of fractional Debye type dipole process varies between g_d to 2-g_d below and above the loss peak and also depends on dielectric strength $(\Delta \epsilon)_{G_+}$. On the right panel in Fig. 3, Debye type dipole dielectric loss and fractional Debye type dielectric loss for $g_d=0.4$ are shown with Debye relaxation time (1s). The magnitudes of slow and fast relaxation times are 5.99 and 0.167(s) respectively and these shown as red and blue dots on the lines for $g_d=0.4$.

4. Dielectric loss data analysis

4.1 1-Cyanoadamantane

The dielectric loss data of 1-cyanoadamantane $(C_{10}H_{15}CN, 1-CNA)$ are taken from Lunkenheimer's research group [22,23]. 1-CNA is a simple prototypical plastic crystal with carbon atoms form a cage, the free bonds being saturated by hydrogen atoms and one cyano-group. Below the melting temperature (T_{w} =458 K) the plastic phase is formed and at T=280 K orientational order occurs. The dielectric loss data and schematic view of molecular structure as insets are shown on the top panel in Fig. 4 for the plastic-crystalline phase of 1-CNA. The data are shown as black dots. The data analysis covered on the plastic-crystalline phase having wide measured frequency range up to 20 GHz. Lunkenheimer's research group have performed numerical Fourier transform of KWW function for the temperature dependent data of loss data of 1-CNA and found worse fit and hence they rejected KWW method. Further, the 1-CNA loss data were analyzed using empirical form of CD dielectric functions. For all the temperatures, the loss data did not fit well around two decades at high frequency region.



Fig. 4: Fit results of dielectric loss of a simple van der Waals system plastic crystal 1-cyanoadamentane (1-CNA) for T=280K shown on the top panel, where number of subunits of molecular process n contributed to dielectric loss is 1. The dashed red and blue lines are Debye type dipole dielectric loss G_0 and continuous red and blue lines and shades are fractional Debye type dipole $G_{_}$ and G_{+} dielectric loss and green line and shade is sum of dipoles $G_{-}+G_{+}$ dielectric loss. The estimates of fit parameters (FP) and standard error (SE) are shown as an attachment. The panel in the middle shows temperature dependent loss data of 1-CNA with interaction strength g_{a^+} The $G_{_}$ and G_{+} dipole dielectric loss contributions are shown for T=260K and 420K. The double headed arrow indicates primary relaxation time. Arrhenius type temperature dependence Debye type relaxation time, slow and fast relaxation times are shown in right side of middle panel. The bottom panel shows dielectric strength and interaction strength as function of temperatures.

The fit result based on Eq. (20) is shown in Fig. 4 for 1-CNA loss data, where $\sigma_{dc}=0$, and n is found to be one. The estimate of fit parameters (FP) and standard errors (SE) attached in Fig. 4 of to panel. With simple orientational order, the Debye type dipole G_0 and the interaction originated fractional Debye type dipoles $G_{-}=g_dG_0$ and $G_{+}=(2-g_d)G_0$, with $g_d=0.701$ and their respective dielectric strength shows excellent fitting. During the molecular motion, the instantaneous transfer of Debye type dipole of G_0 of 1-CNA molecule is incomplete by a factor (1- g_d) G_0 , and hence the fractional Debye type dipoles G_{-} and G_{+} relaxation process initiated and fractional Debye type dipole takes over and resulting a spread in Debye type dipole dipole dielectric spectra as shown in Fig. 4. The Debye type dipole are shown as dashed lines and the continuous lines and shades are fractional Debye type dipole relaxation process where $0 < g_d < 1$.

In Fig. 4, the middle panel, the temperature dependence data are further analyzed for wide range of frequency and temperature dependent dielectric loss peaks are shown in form of Arrhenius plot. The straight line fit equation, slope and attempt frequency $1/\tau_0$ are indicated in Fig. 4. The slow and fast relaxation times are shown with Debye type relaxation time. The bottom panel in Fig. 4 shows dielectric strengths $(\Delta \epsilon)_{G_{\perp}}$ and interaction strength g_d as a function of temperature. The proposed model shows excellent fit for the entire region of frequency and provides new physical insight for the molecular motion in terms dipole-dipole interaction with the concept of Debye type and fractional Debye type dipole polarization.

4.2 Dielectric loss data analysis of supercooled glycerol

The dielectric loss data of supercooled glycerol $(C_3H_5(OH)_3)$ are taken from Lunkenheimer's research group [24]. The dielectric spectra and schematic view of molecular structure as insets are shown in Fig. 5 for the super-cooled phase of glycerol on the top panel to demonstrate the typical analysis of dielectric loss data based on Eq. (20). The glass transition temperature of glycerol T_g is 184K. In glycerol system σ_{dc} =0, and the number of subunits n contributing to the dielectric loss is found to be 2. One

of the challenging problems in the dielectric loss spectra is the excess wing in some of the glass forming systems and it is a common-feature without well resolved β relaxation. Lunkenheimer's research group performed high precision aging experiments lasting up to five weeks, and they have shown the equilibrium spectra below T_g , showing up excess wing (long tail above the α peak) as a second power law at high frequencies, developed into a shoulder. Their results strongly suggested that the excess wing, observed in a variety of glass formers, is the high-frequency flank of a β relaxation.

In the present work, we have analyzed the dielectric loss spectra of glass-forming glycerol at temperature above and below T_g based on the proposed model. Typical result



of dielectric loss data of glycerol at 204K is shown in Fig. 5. The number of subunits n=2 is obtained for the dielectric loss data analysis and estimates of fit parameters (FP) and their standard errors (SE) are attached in Fig.5. Excellent fit parameters and fits are obtained for n=2, where there are two closely spaced times scales of motions are observed as two different Debye type dipole moments $(\mathbf{G}_0)_1$ and $(\mathbf{G}_0)_2$ with their corresponding fractional Debye type dipole moments $(\mathbf{g}_d \mathbf{G}_0)_1$ and $((2-\mathbf{g}_d)\mathbf{G}_0)_1$, $(\mathbf{g}_d \mathbf{G}_0)_2$ and $((2-\mathbf{g}_d)\mathbf{G}_0)_2$ where dipole-dipole interaction strengths are $(\mathbf{g}_d)_1=0.264$

and $(g_d)_2=0.670$ and two different Debye type relaxation times are $(\tau_d)_1=2.35\times10^{-2}(s)$, $(\tau_d)_2=7.94\times10^{-3}(s)$. Both Debye type dipoles and fractional Debye type dipoles and their sums are shown as dashed lines and continuous lies. The proposed model predicts the existence of mysterious high frequency flank of a α relaxation, though it is not well resolved in the dielectric loss data explicitly.

Similar fitting procedure is followed for other temperatures [24] and result are reported in the middle panel of Fig. 5. The double arrow around loss peak indicates position of relaxation time $(\tau_d)_1$ and $(\tau_d)_2$. The temperature dependence of $(\tau_d)_1$ and $(\tau_d)_2$ shows VFT features and the VFT fit parameters and fragility are obtained based on Eqs. (25)-(26) as:

 $(\tau_0)_1 = 10^{-12.84\pm0.48}$, $(A_0)_1 = 11.64\pm1.09$, $(T_0)_1 = 140.79\pm2.12$, and the fragility $(m_p)_1 = 70.2$,

 $(\tau_0)_2 = 10^{-14.53\pm0.54}$, $(A_0)_2 = 15.16\pm1.51$, $(T_0)_2 = 133.42\pm2.54$, and the fragility $(m_p)_2 = 63.2$.

The dielectric strength and interaction strength obtained based of fit results of dielectric loss data are shown in bottom panel in Fig.5 for n=1, and 2. The interaction strength for the subunit n=1 of the molecular process is found to be much stronger than n=2, and hence the excess wing or long tail in the dielectric loss is due the slow α process and it is clearly shown in Fig. 5, for T=195 as red dashed line in middle left panel. Figure 6 shows the compiled dielectric loss data of ten different molecular systems based on proposed model at different temperatures. These data were collected from literature and analysed based on the proposed dielectric Eq. (20) and results are shown in Fig. 6. The list below shows dielectric system, temperature in Kelvin, reference, number of



Fig. 6: A compilation of dielectric loss data range of ten materials is shown covering frequency range of 15 decades. The schematic structure of these molecules with serial numbers and temperature of loss data are shown. (1) Propylene carbonate@153 (2) TriPGG (3) Ketoprofen (4) 1-propanol (5) Magnatite (6) Propylene carbonate@160 (7) Orthocarborane (8) Pentachloro-nitrobenzene (9) Meta-carborane (10) Ethanol (11) Glycerol. For each molecular system the number of subunits n of molecular processes contributing to the dielectric loss is indicated. The double headed arrow indicates dielectric loss contribution from both G_{-} and G_{+} . Among G_{-} and G_{+} the dielectric loss contributions, with respect to temperature variation, the dominant contribution is found to be G_{-} as shown in Langevin function Fig. 1.

subunits n associated with molecular process contributing to dielectric loss, interaction strength and type of relaxation process:

- (1) Propylene carbonate@153 [25], (G_±)₁+(G_±)₂+(G_±)₃, (g_d)₁=0.674, (g_d)₂=0.132, (g_d)₃= 0.654, α, β and Boson peak (three pairs of (G_±) loss show fifteen decades of frequency dependence!);
- (2) *TriPGG*@193 [26], $(\mathbf{G}_{\pm})_1 + (\mathbf{G}_{-})_{2'} (\mathbf{g}_d)_1 = 0.549$, $(\mathbf{g}_d)_2 = 0.277$, α and β ;
- (3) *Ketoprofen*@272 [13], (**G**₋)₁+(**G**₋)₂+(**G**₋)_{3'} (g_d)₁=0.631, (g_d)₂=0.893, (g_d)₃=0.204, α, β and γ;
- (4) 1-propanol@107.7 [27], $(\mathbf{G}_{-})_1+(\mathbf{G}_{-})_2+(\mathbf{G}_{-})_3$, $(g_d)_1=0.997$, $(g_d)_2=0.617$, $(g_d)_3=0.411$, Debye, α and β ;
- (5) *Magnatite*@20 [28], (G₁)₁+(G₂)₂, (g_d)₁=0.433, (g_d)₂=0.698, α and β. The real part of ε^{*}_{GG} (ω) is shown as filled plot based on Eqs. (18) & (19).
- (6) Propylene carbonate@160 [24], $(\mathbf{G}_{\pm})_1 + (\mathbf{G}_{\pm})_2$, $(\mathbf{g}_d)_1 = 0.235$, $(\mathbf{g}_d)_2 = 0.667$, α and β ;
- (7) *Ortho-carborane*@163 (*o*-CA) [23], $(\mathbf{G}_{-})_1 + (\mathbf{G}_{\pm})_{2'} (g_d)_1 = 0.882$, $(g_d)_2 = 0.450$, α and β ;
- (8) Pentachlornitrobenzene@350 [23] $(g_d)_1$ =1.0, $(g_d)_2$ =0.805, α and β ;
- (9) *Meta-carborane*@252 (*m*-CA) [23], $(\mathbf{G}_{-})_1 + (\mathbf{G}_{-})_2$, $(g_d)_1 = 1.0$, $(g_d)_2 = 0.787$, α and β ;
- (10) *Ethanol*@231 [29], $(G_{-})_{1'}$, $(g_{d})_{1}$ =0.943, α ;
- (11) *Glycerol*@363 [25], $(\mathbf{G}_{\pm})_1 + (\mathbf{G}_{-})_{2'} (\mathbf{g}_d)_1 = 0.557, (\mathbf{g}_d)_2 = 1.0, \alpha$ and β .

5. Summary and conclusions

The existing time-honoured NDR functions with their exponents, $\beta_{KWW'}\,\alpha_{_{CC'}}\,\beta_{_{CD'}}\,(\alpha_{_{HN'}}\,\beta_{_{HN}})$ and (m,n) were introduced 163, 76, 66, 50, and 43 years ago respectively. Still their use in dielectric loss analysis is piecemeal approach tailored to individual materials and often highly arbitrary. The proposed Eqs. (20)-(24) have polarization relaxation dynamics of Debye type dipole G_0 and fractional Debye type dipoles $\pm G$, and G_{+} , where $\pm G = (1-g_d)G_{0'}$ $\mathbf{G}_{-}=\mathbf{G}_{0}-(1-g_{d})\mathbf{G}_{0}=g_{d}\mathbf{G}_{0'}\mathbf{G}_{+}=\mathbf{G}_{0}+(1-g_{d})\mathbf{G}_{0}=(2-g_{d})\mathbf{G}_{0}$ and these dipoles will open a window on one of Nature's bestkept secrets of NDR. The proposed model will heighten the understanding of NDR and physical insight for the dielectric loss of α , β and γ relaxations, excess wing, and closely related ac conductivity and mechanical relaxation. Hopefully, the proposed fractional Debye type model will be able to unify and encompass the existing NDR approach with an amendments. The universal Debye type dipole relaxation and its associated fractional Debye type dipole relaxation dynamics with redistribution and

conservation of moment and energy in the storage and dissipation processes in the dielectric response are too striking and believed that one underlying principle of "molecular level many-body interactions between its constituent parts" governs the response of condensed matter to electromagnetic fields.

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