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Unique Dielectric Dipole and Hopping Ion Dipole Relaxation in Disordered Systems

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Abstract. Dielectric or ac conductivity measurements of dielectric and ion conducting glass and crystalline systems provide considerable insight into the nature of the dipolar and ionic motions in disordered solids. However, interpreting the dielectric or ac conductivity has been a matter of considerable debate based on the existing models and empirical formalism, particularly in regards to how best to represent the relaxation process that is the result of a transition from correlated to uncorrelated dipolar and ionic motions. A unique dipole interaction process has been proposed for the (a) dielectric dipole process (b) the hopping ion conducting dipole process and the (c) combination (a) and (b) for the description of dielectric spectra and ac conductivityspectra and results are reported.

INTRODUCTION

The dielectric and conductivity spectra of wide range of systems prove the existence of remarkable features of frequency and time response which is basically incompatible with the variety of currently used, time-honored (i) Cole-Cole [1] (ii) Cole-Davidson [2] (iii) Havriliak-Negami[3] dielectric functions (iv) Kohlrausch-Williams-Watts stretched exponential function [4] (v) Jonscher's universal dielectric response [5] (vi) Ngai's coupling model[6] (vii) Dyre's random energy barrier model [7]. (viii) Funke's mismatch relaxation processes [8] (ix) Sidebottom's anomalous relaxation process [9]. The existinginterpretations for these models are: (a)distributions of relaxation times and (b) the tentative 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 paperis to present a novel concept of "Debye type dipole and Debye type fractionaldipole" relaxation process to the interpretation of the dielectric spectra and ac conductivity spectra of disordered solids. The dielectric relaxation and conductivity relaxation processes is based on Debye type dipole-dipole interaction driven Debye type fractional 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 conductivity functions, and their energy criterion in terms of Debye dipole and Debye type fractionaldipoleprocess provides a new physical insight for the dielectric and ac conductivity relaxations. The dielectric spectra of glass formers and conductivity spectra of disordered system are analyzed and new physical insight for the description of dielectric process in condensed matter systems reported.The model shows excellent agreement with experimentally observed dielectric spectraand conductivity spectra of wide variety of materials.

DIELECTRIC AND CONDUCTION DIPOLE PROCESSES

Let the condensed matter system consist of (a) the reorientation of dipolar entities with dipole moment $(\mu_0)_d$ and (b) hopping charge polarization with dipole moment$(\mu_0)_c$, where $(\mu_0)_d$, and $(\mu_0)_c$are Debye type dipoles (non-interacting) and also known as "free dipole"in dielectric dipole process and "pinned dipoles" in conduction dipole

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process respectively,where the suffix d stands for dielectric and c for conduction dipoles processes [10-13]. In a condensed matter dielectric system, dielectric dipole and conduction dipoles are in motion and under a given thermodynamic condition the dipole moment transfer *cannot* take place instantaneously during motion for a given molecule due to intermolecular interactions and environment of the dipole, and hence the*Debye type fractional dipoles*:

$$(\boldsymbol{\mu})_{d,c}=((1-\alpha)\boldsymbol{\mu}_0)_{d,c},\ (\boldsymbol{\mu}_-)_{d,c}=(\boldsymbol{\mu}_0-\boldsymbol{\mu})=(\alpha\boldsymbol{\mu}_0)_{d,c},\ (\boldsymbol{\mu}_+)_{d,c}=(\boldsymbol{\mu}_0+\boldsymbol{\mu})_{d,c}=((2-\alpha)\boldsymbol{\mu}_0)_{d,c} \tag{1}$$

are created in terms of $\boldsymbol{\mu}_0$, where $0<\alpha_{d,c}<1$. The Debye type dipole $\boldsymbol{\mu}_0$evolves with Debye type fractional dipole $\boldsymbol{\mu}$ and becomes$\boldsymbol{\mu}_\pm$dipoles and it is defined as *non-Debye dipoles*, N number of $\boldsymbol{\mu}_0$, and becomes N/2 number of $\boldsymbol{\mu}_\pm$ pairs.There is growth and shrinkage of Debye type dipole strength$\boldsymbol{\mu}_0$ by an amount $(1-\alpha)\boldsymbol{\mu}_0$. The magnitude of $(1-\alpha)\boldsymbol{\mu}_0$ depends on system and thermodynamic condition. The energy of $\boldsymbol{\mu}_+$ and $\boldsymbol{\mu}_-$is increased and decreased respectively by a factor of $(1-\alpha)$, where α signifies strength of interaction. The polarization relaxation dynamics with effect of $\boldsymbol{\mu}$ on $\boldsymbol{\mu}_0$ defines the deviation from Debye feature and it is called as non-Debye relaxation (NDR). The dipole$\{\boldsymbol{\mu}_0, \boldsymbol{\mu}, \boldsymbol{\mu}_\pm\}_{d,c}$bunchis referred as GG dipoles.

The potential energy of the dipoles $\boldsymbol{\mu}_0$, $\boldsymbol{\mu}_-$and $\boldsymbol{\mu}_+$in the presence of external field **F**is $U_i=G_iF\cos(\theta_i)$, where θ_i is angle between dipole moment and applied electric field **F**, and $i=0$and $i=\pm$ refer Debye type and non-Debye dipoles. The average value of dipole moment $\boldsymbol{\mu}_0$, $\boldsymbol{\mu}_-$, and $\boldsymbol{\mu}_+$ in direction field **F** is obtained using Langevin function [5]:

$$<\boldsymbol{\mu}_i>= \mu_i L(z_i),\ L(z_i)=\coth(z_i)-1/z_i \tag{2}$$

where$z_i= \mu_i F/(k_B T)$, the symbol <> stands for the Boltzmann statistical ensemble average, and for $\mu_0 F<<k_B T$, $L(z_i)= z_i/3$, $<\mu_i>=\mu_i L(z_i)=\mu_i^2 F/3k_B T$.The permanent dipole moment $\boldsymbol{\mu}_0$ for multi-atomic molecules is not independent of temperature because in this case, the permanent dipole moment is the result of several moments, and their internal reorientation is dependent on their individual activation energies and hence on the temperature.The value of $L(z_-)$ is less than the value of $L(z_0)$ and the value of $L(z_+)$ is greater than the value of $L(z_0)$ at the given ratio of electrical energy of dipole to the thermal energy. The magnitude of Langevin function $L(z_-)$ and $L(z_+)$ is a function of $(\alpha)_{d,c}$. For large value of z_0, functions $L(z_-)$, $L(z_0)$ and $L(z_+)$ approach to one, however, depends on $(\alpha)_{d,c}$. Since the energy and moment of the Debye dipole $\boldsymbol{\mu}_0$, areredistributed through, $\boldsymbol{\mu}_-$, and $\boldsymbol{\mu}_+$, the statistical distribution of dipoles through the Boltzmann factor$exp[-(U_i/k_BT)]$ is different for $\boldsymbol{\mu}_-$, and $\boldsymbol{\mu}_+$, when compared with the Debye dipole $\boldsymbol{\mu}_0$. The redistribution of energy and moment among the $\boldsymbol{\mu}_-$, and $\boldsymbol{\mu}_+$ is coupled and correlated to Debye dipole $\boldsymbol{\mu}_0$ in terms of the fraction $(\alpha)_{d,c}$.

Let us consider non-Debye spectra of a disordered system having dispersion contributions from both dielectric dipole pair and conductive dipole pair processes, then, the total complex permittivity of the system is given by:

$$\epsilon_{GG}^*(\omega)=\sum_{m=1}^{n}([\epsilon_d^*(\omega)]_{\mu_+}+[\epsilon_d^*(\omega)]_{\mu_-})_m+[\epsilon_c^*(\omega)]_{\mu_+}+[\epsilon_c^*(\omega)]_{\mu_-} \tag{3}$$

where$\epsilon_d^*(\omega)$is the dielectric dipole contribution to complex permittivity, the sum m takes care of n number of subunits or subgroups or sub-clusterscontributions of a molecule and $\epsilon_c^*(\omega)=\sigma_c^*(\omega)/i\omega\epsilon_0$ is the hopping ion conductiondipole process contribution to the complex dielectric. Other ac electrical representations are (i) complex conductivity$\sigma_{GG}^*(\omega)=1/\rho_{GG}^*(\omega)=i\omega\epsilon_0\epsilon_{GG}^*(\omega)$ (ii) complex electric modulus $M_{GG}^*(\omega)=1/\epsilon_{GG}^*(\omega)$.

The complex dielectric function$[\epsilon_d^*(\omega)]_{\mu_-}$for the $\boldsymbol{\mu}_-=\alpha_d\boldsymbol{\mu}_0$ is obtained by incorporating the consequence of $\boldsymbol{\mu}=(1-\alpha_d)\boldsymbol{\mu}_0$ on $\boldsymbol{\mu}_0$, where $[\epsilon_d^*(\omega)]_{\mu_0}$is the Debye complex dielectric function. The influence of $\boldsymbol{\mu}$ on the Debye type complex dielectric $[\epsilon_d^*(\omega)]_{\mu_0}(\alpha_d=1)$ is shifting of the Debye term, $i\omega\tau_d$, by a factor of $1/(i\omega\tau_d)^{1-\alpha_d}$, and hence the Debye term, $i\omega\tau_d$ becomes non-Debye dipole $\boldsymbol{\mu}_-$term $i\omega\tau_d/(i\omega\tau_d)^{1-\alpha_d}=(i\omega\tau_d)^{\alpha_d}$. In terms of energy, the Debye dipole energy is *decreased* by a factor of $(1-\alpha_d)$. The complex permittivity function$[\epsilon_d^*(\omega)]_{\mu_-}$ for $\boldsymbol{\mu}_-$ is obtained as:

$$[\epsilon_d^*(\omega)]_{\mu_-}-\epsilon_\infty=\frac{(\Delta\epsilon)_{\mu_0}}{1+(i\omega\tau_d)^{\alpha_d}}=\left(\frac{\Delta\varepsilon}{1+S\Gamma}\right)_{\mu_-}, \tag{4}$$

where$S_{\boldsymbol{\mu}_-} = \frac{s}{s^{1-\alpha_d}}$, $\Gamma_{\boldsymbol{\mu}_-} = \tau_d^{\alpha_d}$, $s = i\omega$, and

$$(\Delta\epsilon)_{\boldsymbol{\mu}_0} = (\epsilon_s - \epsilon_\infty)_{\boldsymbol{\mu}_0} = \frac{N}{2}\frac{\mu_0^2}{3\epsilon_0 k_B T} - \epsilon_\infty, \tag{5}$$

is the dielectric strength of $\boldsymbol{\mu}_-$, ϵ_s and ϵ_∞ are the high and low external frequency permittivity limits respectively, N is the dipole density. This is similar but not same as Cole-Cole type complex dielectric function.

The complex dielectric function $[\epsilon_d^*(\omega)]_{\boldsymbol{\mu}_+}$ for the non-Debye dipole $\boldsymbol{\mu}_+=(2-\alpha_d)\boldsymbol{\mu}_0$ is obtained by incorporating the consequence of $\boldsymbol{\mu}=-(1-\alpha_d)\boldsymbol{\mu}_0$ on $\boldsymbol{\mu}_0$, where $[\epsilon_d^*(\omega)]_{\boldsymbol{\mu}_0}$, is the Debye complex dielectric function. The influence of $\boldsymbol{\mu}$ on Debye complex dielectric function$[\epsilon_d^*(\omega)]_{\boldsymbol{G}_0}$, ($\alpha_d=1$) is the shifting of the Debye terms, $i\omega\tau_d$ by a factor of $1/((-i)\omega\tau_d)^{-(1-\alpha_d)}$ and hence the Debye term, $i\omega\tau_d$ becomes $i\omega\tau_d/((-i)\omega\tau_d)^{-(1-\alpha_d)} = i^{\alpha_d}(\omega\tau_d)^{2-\alpha_d}$, since $(-i)^{-(1-\alpha_d)} = i^{(1-\alpha_d)}$. The complex dielectric function$[\epsilon_d^*(\omega)]_{\boldsymbol{\mu}_+}$ for non-Debye dipole $\boldsymbol{\mu}_+$ is obtained as:

$$[\epsilon_d^*(\omega)]_{\boldsymbol{\mu}_+} = \frac{(\Delta\epsilon)_{\boldsymbol{\mu}_0}}{1+i^{\alpha_d}(\omega\tau_d)^{2-\alpha_d}} = \left(\frac{\Delta\varepsilon}{1+S\Gamma}\right)_{\mu_+}, \tag{6}$$

where $S_{\boldsymbol{\mu}_+} = \frac{s}{(-s)^{-(1-\alpha_d)}}$, $\Gamma_{\boldsymbol{G}_+} = \tau_d^{2-\alpha_d}$, $s = i\omega$,

$$(\Delta\epsilon)_{\boldsymbol{\mu}_0} = (\epsilon_s - \epsilon_\infty)_{\boldsymbol{\mu}_0} = \frac{N}{2}\frac{\mu_0^2}{3\epsilon_0 k_B T} - \epsilon_\infty. \tag{7}$$

The energy and moment of the dipole $\boldsymbol{\mu}_-$ and $\boldsymbol{\mu}_+$ is shifted with respect to $\boldsymbol{\mu}_0$, in equal magnitudes, and the total energy and moment of the system is conserved. Since, the energy of Debye dipole $\boldsymbol{\mu}_0$ is redistributed through the non-Debye dipole pair $\boldsymbol{\mu}_\pm$, the dielectric loss spreads in the complex dielectric function.

The terms$[\epsilon_c^*(\omega)]_{\boldsymbol{\mu}_+}$ and $[\epsilon_c^*(\omega)]_{\boldsymbol{\mu}_-}$in Eq. (3) are given by

$$(i\omega\epsilon_0)[\epsilon_c^*(\omega)]_{\boldsymbol{\mu}_+,\boldsymbol{\mu}_-} = [\sigma_c^*(\omega)]_{\boldsymbol{\mu}_-} + [\sigma_c^*(\omega)]_{\boldsymbol{\mu}_+}, \tag{8}$$

Expressions for $[\sigma_c^*(\omega)]_{\boldsymbol{\mu}_-}$, and $[\sigma_c^*(\omega)]_{\boldsymbol{\mu}_+}$ are obtained following procedure of dielectric non-Debye dipoles. Replacing τ_d, g_d by τ_c, g_c, we obtain:

$$(i\omega\epsilon_0)[\epsilon_c^*(\omega)]_{\boldsymbol{\mu}_-} = \sigma(0)(1 + (i\omega\tau_c)^{\alpha_c}), \tag{9}$$

$$(i\omega\epsilon_0)[\epsilon_c^*(\omega)]_{\boldsymbol{\mu}_+} = \sigma(0)(1 + i^{\alpha_c}(\omega\tau_c)^{2-\alpha_c}), \tag{10}$$

$$[(i\omega\epsilon_0)\epsilon_c^*(\omega)]_{\boldsymbol{\mu}_0} = \sigma(0)(1 + i\omega\tau_D), \tag{11}$$

whereτ_c is the hopping ion conductivity relaxation time, $0<\alpha_c<1$ signifies interaction strength in the conductivity process.

The depolarization relaxation function for non-Debye dipole pair$\boldsymbol{\mu}_-$and $\boldsymbol{\mu}_+$ is obtained by accommodating the consequence of $\boldsymbol{\mu}$ on the Debye dipole relaxation function $\boldsymbol{\mu}_0$, and these are given by:

$$P_{GG}(t) \propto (\textstyle\sum_{m=1}^{n}([P_d(t)]_{\boldsymbol{\mu}_-} + ([P_d(t)]_{\boldsymbol{\mu}_+})_m + [P_c(t)]_{\boldsymbol{\mu}_-} + [P_c(t)]_{\boldsymbol{\mu}_+}) \tag{12}$$

where

$$[P_d(t)]_{\boldsymbol{\mu}_-} \propto exp\left[-\left(\frac{t}{\tau_d}\right)^{\alpha_d}\right]; [P_d(T)]_{\boldsymbol{\mu}_-} \propto exp\left[-\left(\frac{T}{\Gamma}\right)_{\boldsymbol{\mu}_-}\right],\ T_{\boldsymbol{\mu}_-} = t^{\alpha_d}, \tag{13}$$

$$[P(t)]_{\boldsymbol{\mu}_+} \propto exp\left[-\left(\frac{t}{\tau_d}\right)^{2-\alpha_d}\right];[P_d(T)]_{\boldsymbol{\mu}_+} \propto exp\left[-\left(\frac{T}{\Gamma}\right)_{\boldsymbol{\mu}_+}\right],\ T_{\boldsymbol{\mu}_+} = t^{2-\alpha_d}. \tag{14}$$

These are time domain non-Debye dipole dielectric polarization relaxation functions corresponding to the frequency domain non-Debye dipole complex dielectric functions (Eqs. (4) & (6)). The third and fourth terms of Eq. (12)isthe polarization relaxation function of hopping ion conductionnon-Debye dipoles and these are given by:

$$[P_c(t)]_{\mu_-} \propto exp\left[-\left(\frac{t}{\tau_c}\right)^{\alpha_c}\right];\ [P_c(T)]_{\mu_-} \propto exp\left[-\left(\frac{T}{\Gamma}\right)_{\mu_-}\right],\ T_{\mu_-} = t^{\alpha_c}, \tag{15}$$

$$[P_c(t)]_{\mu_+} \propto exp\left[-\left(\frac{t}{\tau_c}\right)^{2-\alpha_c}\right];[P_c(T)]_{\mu_+} \propto exp\left[-\left(\frac{T}{\Gamma}\right)_{\mu_+}\right],T_{\mu_+} = t^{2-\alpha_c}. \tag{16}$$

In frequency domain the imaginary part of the relaxation functions$[\epsilon_d^*(\omega)]_{\mu_-}$or $[\epsilon_d^*(\omega)]_{\mu_+}$ or $[\epsilon_d^*(\omega)]_{\mu_-}+[\epsilon_d^*(\omega)]_{\mu_+}$are related to the energy loss due to the relaxation response of dipoles. The energy loss is pronounced when the frequency is close to a typical relaxation time in the system and imaginary part thus exhibits a peak. For the dielectric energy loss for Debye dipole μ_0 is maximum at $\tau_d=\tau_D=1/\omega_D$ ($\alpha_d=1$), where ω_D is the Debye peak frequency. Equating the dielectric energy loss of Debye dipole μ_0 with dielectric energy loss of$[\epsilon_d^*(\omega)]_{\mu_-}$or $[\epsilon_d^*(\omega)]_{\mu_+}$ or $[\epsilon_d^*(\omega)]_{\mu_-}+[\epsilon_d^*(\omega)]_{\mu_+}$at $\omega=1/\tau_{d,c}$ provides slow relaxation time and fast relaxation for the non-Debye relaxation processes with respect to the Debye relaxation frequency$\tau_D=1/\omega_D$and these are given by:

$$\tau_s^* = \tau_D\{\cot(\alpha_{d,c}\pi/4) + \sqrt{\cot^2(\alpha_{d,c}\pi/4) - 1}\}, \tag{17}$$

$$\tau_f^* = \tau_D\{\cot(\alpha_{d,c}\pi/4) - \sqrt{\cot^2(\alpha_{d,c}\pi/4) - 1}\}, \tag{18}$$

where $\cot(\alpha_{d,c}\pi/4)$ is a non-Debye dipole relaxation loss tangent of $[\epsilon_d^*(\omega)]_{\mu_-}$or $[\epsilon_d^*(\omega)]_{\mu_+}$or $[\epsilon_d^*(\omega)]_{\mu_-}+[\epsilon_d^*(\omega)]_{\mu_+}$, at loss peak $\omega=1/\tau_d$. Interestingly, the slow relaxation time, τ_s^* and fast relaxation time τ_f^*, is function of α_d and they become the Debye dielectric relaxation time at the loss peak frequency when $\alpha_d=1$.

DIELECTRIC SPECTRA DATA ANALYSES

The dielectric spectra of super-cooled liquids reveal several relaxation features, which are believed to be the key to achieve a better understanding of the glass transition [14,15,16]. The most noticeable of them is the well-known α relaxation or structural relaxation characterized by strong non-Arrhenius dependence of the relaxation time on temperature. In addition, all glass formers reveal fastersecondary relaxation and it is known as β relaxation orJohari-Goldstein (JG) relaxation processes [17]. In some systems, β appears as awell-defined peak at higher frequencies than the α-peak indielectric loss spectra and they are known as type B systems [18]or in certain systems β appears as an excesswing (EW)[19-24] on the high-frequency flank of the structural relaxation and these are known as type A. The origin of theEW is still controversial in the literature [20-23]. The dielectric relaxation of super-cooled glycerol ($C_3H_5(OH)_3$) have been measured by many investigators [15,16] and still the different relaxation processes and EW are debated. We elucidate some of these issue by analyzing the dielectric spectra of glycerol in the frequency range of 9 decades over 16 different temperatures from 192K to 252K in steps of 4K using our proposed model. These data are available in the JeppeDyre's research group website [25,26] for those who are interested in theoretical interpretation or for testing new theoretical model. These dielectric spectra data are analyzed based on the proposed Eqs.(3) and (12).

In a system like glycerol, there is no hopping ion conduction dipole contribution to total complex dielectric function Eq. (7), however, pure dc conduction $\sigma_{dc}$is observed at high temperature. Since the potential energy of the Debye dipole μ_0 and μ_- is less compared with potential energy μ_+, the Boltzmann factor $exp[-(U_i/k_BT)]$ is higher for μ_0, and μ_-, when compared with μ_+. Therefore, in general, $[\epsilon_d^*(\omega)]_{\mu_+}=0$ (not always), and the dielectric contribution is dominant by the term ($[\epsilon_d^*(\omega)]_{\mu_-}$.When the spectra show free charge dc conductivity σ_{dc}contributionat elevated temperatures, the free charge dc conductivity contribution term$\sigma_{dc}/(i\omega\varepsilon_0)$ will be added.Therefore,total complex dielectric function Eq. (3) for the glycerol becomes:

$$\epsilon^*_{GG}(\omega) = \sum_{m=1}^{n}([\epsilon^*_d(\omega)]_{\boldsymbol{\mu}_-})_m + \sigma_{dc}/(i\omega\epsilon_0). \qquad (19)$$

The glycerol dielectric loss, $\epsilon''_{GG}(\omega)$, and dielectric real part, $\epsilon'_{GG}(\omega)$, are analyzed in the temperature range 192 to 252K in steps of 4K using Eq. (19), and theresult of the fitting are shown in log-log plot in Fig. 1(a)-(b), where(a) is dielectric loss and (b) is real part of dielectric spectra. The green lines indicate result of the fittingand black dots are measured data.The schematic molecular structure of glycerol is shown as inset in Fig. 1(b). In the sketch of the molecular structures, the oxygen atom is highlighted in red. From low to high temperatures, the number of subunits or sub-clusters of molecule n contributed to the $\epsilon''_{GG}(\omega)$are: n=4 in T=192-224K range; n=3 in T228-232K range; n=2 in T=236-244K range; n=1 in T= 248-252K range. The value of the n depends on the nature of the molecule and the temperature, and at elevated temperaturesweaker dipoles do not contribute to loss spectra.The temperature dependence of interaction strength $(\alpha_d)_m$, dielectric strength $(\Delta\varepsilon)_m$, and sum of $(\Delta\varepsilon)_m$andε_∞, and relaxation times $(\tau_d)_m$ (m=1,2,3,4) are shown in Figs. 2(a), (b) & (c) respectively.

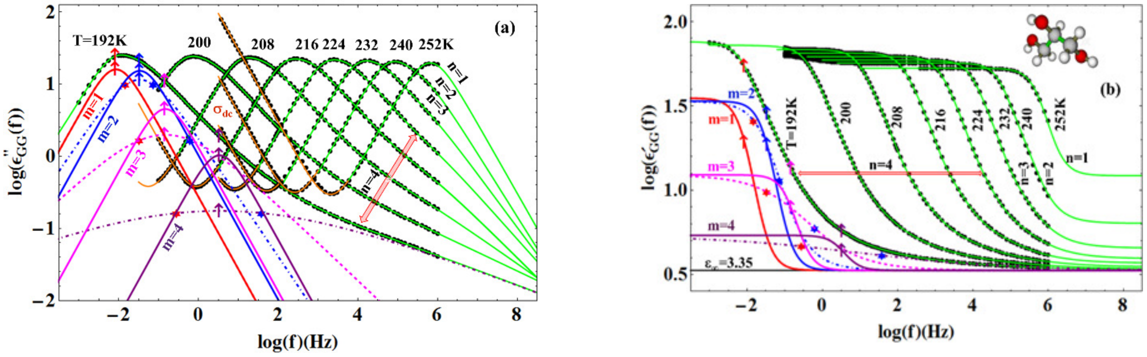

FIGURE 1. (a) The green lines are fit results of dielectric loss and (b) dielectric constant of glycerol as a function of frequency obtained based on Eq. (19) for n=4, 3, 2, 1 for T=192-252K. The black dots are measured data [24, 25].For T=192K, the arrows indicate relaxation time: m=1, Debyetype process relaxationtime $(\tau_d)_1$; m=2, non-Debye dipoleα relaxation time $(\tau_d)_2$; m=3, β relaxation time$(\tau_d)_3$; m=4, γ relaxation time $(\tau_d)_4$ of subunitsof molecular motions. The slow and fast relaxation times $(\tau_S^*)_{1,2,3,4}$ and $(\tau_f^*)_{1,2,3,4}$ are shown as red and blue stars.The red, blue, magenta and purple lines, dashed and dot-dashed lines are Debye and non-Debye dipole dielectric loss with loss peak at$(\tau_d)_{1\text{-}4}$. The orange portion of line in Fig 1(a) is the σ_{dc} contribution.

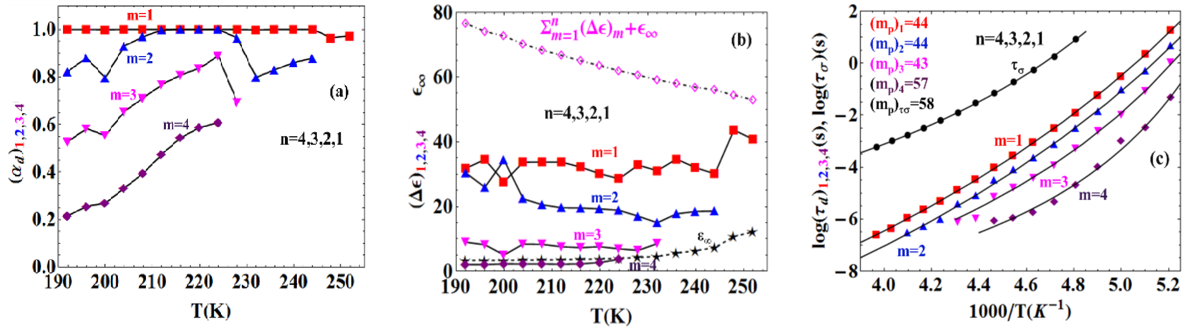

FIGURE 2. Temperature dependence of (a) $(\alpha_d)_1$-$(\alpha_d)_4$,(b) $(\Delta\varepsilon)_1$-$(\Delta\varepsilon)_4$, sum of $(\Delta\varepsilon)_{1,2,3,4}$and ε_∞ (star symbol); and(c) $(\tau_d)_1$-$(\tau_d)_4$, $\tau_\sigma=\varepsilon_0\varepsilon_\infty/\sigma_{dc}$obtained based on Eq. (19) for glycerol. In (a) and (b) lines guide to eye. The fit results based on Eq. (20) for $(\tau_d)_1$-$(\tau_d)_4$, andτ_σ show VFT feature. The fragility index$(m_p)_{1\text{-}4}$ and$(m_p)_{\tau\sigma}$ obtained based on Eq. (21) are shown in Fig. 2(c).

Thered, blue, magenta and purple arrows on the curve in Fig. 1 (a) &(b) for T=192K, indicate $(\tau_d)_n$(n=1,2,3,4) in decreasing order. Four different Debye dipole and their corresponding non-Debye dipole processes are shown as red, blue, magenta and purple lines and dashed & dot dashed lines in Fig. 1(a) & (b) for $(\tau_d)_n$(n=1,2,3,4) and Table 1 shows fit parameter for these processes and (τ_S^*) &(τ_S^*) calculated using Eqs. (17) & (18).It is clear from Figs. 1(a) &

(b), the shape of $\epsilon''_{GG}(\omega)$ depends on the relaxation times $(\tau_d)_1$-$(\tau_d)_4$, the magnitude of dielectric strength $(\Delta\varepsilon)_1$-$(\Delta\varepsilon)_4$ and interaction strength $(\alpha_d)_1$-$(\alpha_d)_4$.

TABLE 1. Fit parameters for T=192K obtained based on Eq.(19) for n=4.

m	$(\alpha_d)_m$	$(\Delta\varepsilon)_m$	$(\tau_d)_m$(s)	$(\tau_s^*)_m$(s)	$(\tau_f^*)_m$(s)
1	1.000	31.81	18.62	0.00	0.00
2	0.823	30.39	4.72	10.36	2.15
3	0.527	8.99	1.07	4.65	0.25
4	0.214	2.05	0.05	0.55	0.004

ε_∞=3.35.

In glycerol, n=4, in T=192-224K range, relaxation times $(\tau_d)_1$-$(\tau_d)_4$ are closely spaced (for example $(\tau_d)_1/(\tau_d)_4$~250, whereas, in the case of 2-ethyle-1-hexanol, $C_8H_{17}OH$, n=4, in T=157-165.5K range, $(\tau_d)_1$-$(\tau_d)_4$ are well separated [11], for example $(\tau_d)_1/(\tau_d)_4$~10^6, results are not shown here). This is the first report showing 4 different closely spaced relaxation times in glycerol and the slowest motion is a Debye type dipole $(\mu_0)_1$relaxation, $(\alpha_d)_1$=1, for all the temperatures, as observed in several classes of hydrogen-bonded liquids [6].Then, as per the existing nomenclatures, $(\tau_d)_1$-$(\tau_d)_4$, are Debye, α, β, and γ relaxations respectively. Therefore, new physical insights based on the proposed model are that the Debye type relaxation is $(\tau_d)_1$, the structural α relaxation is $(\tau_d)_2$,mysteriousβ relaxation is $(\tau_d)_3$ and γ relaxationsis $(\tau_d)_4$ and these describe the motions of subunits or sub-clusters of polar groups having different dipole strengths with ($0<\alpha_d<1$) and without ($\alpha_d=1$) intermolecular dipole-dipole interactions.

The relaxation time of glass former glycerol shows a deviation from Arrhenius law and it is parameterized with Vogel-Fulcher-Tamman (VFT) equation [27] as:

$$(\tau_d)_m=(\tau_0\exp(A_0T_0/(T-T_0)))_m,\ \text{for } T>T_g, \qquad (20)$$

wherem=1, 2, …, n, 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 [27],

$$(m_p)_m=\log_{10}(e)(A_0(T_0/T_g)(1-T_0/T_g)^{-2})_m, \qquad (21)$$

where$T_g$is glass transition temperatureand its value for glycerol is 193K [25],T_0 and A_0 are VFT parameters. The fragility index $(m_p)_{1,2,3,4}$, m_σ for $\tau_\sigma=\varepsilon_0\varepsilon_\infty/\sigma_{dc}$are found from VFT parameters.

Now, what is EW in the proposed model? Is EW a different phenomenon altogether? Is EW high frequency flank of loss peak caused by β or γ? According to the proposed model, whenever, relaxation times of the sub units$(\tau_d)_m$(m=1, 2, 3,..n or α, β, γ, ..) are well separated and if the interaction strength is weak ($(\alpha_d)_m\gtrsim0.6$), the loss peak is observed and, therefore, there is no EW. On the other hand, when $(\tau_d)_m$ are closely spaced and if the interaction strength is strong ($(\alpha_d)_m\lesssim0.6$), loss peaks are merged and EW is observed, as in glycerol in Fig. 1(a) at low temperatures. The extent of EW depends on the interaction strength $(\alpha_d)_m$, closeness of $(\tau_d)_m$, and $(\Delta\varepsilon)_m$. Therefore, EW is not a different phenomenon, and it is high frequency flank of loss peak caused by α or β orγ.

SUMMARY AND CONCLUSIONS

The idea of coupled form of Debye type dipole with shrinkage and growth by a factor of Debye type fractional dipole is introduced for the description of dielectric dipole (“free dipole”) and hopping ion conducting dipole (“pinned dipole”) processes, where the fraction is lying $0<\alpha_{d,c}<1$. The model is generalin terms molecular subunits or sub-clusters dipole-dipole interaction, where the subunits or sub-clusters have different dipole strength. The proposed model with Eqs. (3) and (12) is based on the profound physical principle of the conservation of energy, moment and charge. New physical insights observed in the dielectric spectra of glycerol based on the proposed model are: (i) The number of subunits or sub-clusters n=1,2,3,4 with differing dipole moments $(\mu_0)_{1,2,3,4}$of molecular motions contribute to dielectric spectra from high temperature to low temperature and their variation in temperatures. (ii) Around T_g (193K) the number of subunits n is large and it decreases with increase of temperature.(iii) The slowest relaxation is Debye type relaxation showing VFT features (iv) In addition to Debye type relaxation, three more closely spaced relaxation motionsare observed with varying dielectric strengths with increasing interaction strength around T_g showing VFT feature (v) The sum of different process dielectric strengths decreases with increase of temperature (vi) EW is not a new phenomenon, it is the high frequency tail of high frequency α or β orγ relaxations depending on the temperature and interaction strength.

The non-Debye dipole process proposed in the model will open window of one of the Nature's best-kept secrets of non-Debye relaxation. 169 years oldKohlrausch's fraction $0<\beta<1$, 76 yearsold Cole-Cole's fraction$0<\alpha_{CC}<1$,66 years oldCole-Davidson's fraction$0<\beta_{CD}<1$, 50years oldJonscher'spower law fractionsn, and m ($\omega^{n-1}\leftrightarrow t^{-n}$, $0<n,m<1$, $\omega^{m}\leftrightarrow t^{-m-1}$) were criticized and their use is still debatable [6-9]. We have shown the fraction$\alpha_{d,c}$connecting molecular motion and it can encompass and amend the existing models. The non-Debye dipole in terms of fraction $\alpha_{d,c}$exhibits a common response to ac electrical fields with Debye process as a primary, and slow and fast relaxation times$\tau_s^*$and τ_f^*as secondary process is far more general and connects (i) complex conductivity(ii) complex impedance or resistivity (iii) complex electric modulus.The model can explain dielectric and ac electrical relaxation of (i) all possible polarizing species; dipoles [11,12], hopping ions, electrons, holes [13] (ii) all types chemical bonds and (iii) all structural forms like single crystals, polycrystallineaggregates, glassy and amorphous materials. The universal dielectric and conductive Debye and non-Debye dipoles with their energy and moment redistribution and conservation, and their relaxation dynamics are too striking and believed that one underlying principle governs the response of condensed matter to applied ac electric fields.

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