Characteristics of the secondary relaxation process in soft colloidal suspensions

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Abstract – A universal secondary relaxation process, known as the Johari-Goldstein (J-G) β-relaxation process, appears in glass formers. It involves all parts of the molecule and is particularly important in glassy systems because of its very close relationship with the α-relaxation process. However, the absence of a J-G β-relaxation mode in colloidal glasses raises questions regarding its universality. In the present work, we study the microscopic relaxation processes in Laponite suspensions, a model soft glassy material, by dynamic light scattering (DLS) experiments. α- and β-relaxation timescales are estimated from the autocorrelation functions obtained by DLS measurements for Laponite suspensions with different concentrations, salt concentrations and temperatures. Our experimental results suggest that the β-relaxation process in Laponite suspensions involves all parts of the constituent Laponite particle. The ergodicity breaking time is also seen to be correlated with the characteristic time of the β-relaxation process for all Laponite concentrations, salt concentrations and temperatures. The width of the primary relaxation process is observed to be correlated with the secondary relaxation time. The secondary relaxation time is also very sensitive to the concentration of Laponite. We measure primitive relaxation timescales from the α-relaxation time and the stretching exponent (β) by applying the coupling model for highly correlated systems. The order of magnitude of the primitive relaxation time is very close to the secondary relaxation time. These observations indicate the presence of a J-G β-relaxation mode for soft colloidal suspensions of Laponite.

Introduction. – The exact nature of the relaxation processes in complex, disordered and out-of-equilibrium systems is one of the many unsolved problems in non-equilibrium statistical mechanics. The plethora of non-equilibrium systems around us supply several opportunities to observe diverse fascinating phenomena. The physics of relaxation processes in glasses or glassy systems has been meticulously studied during the last century. It has been noted that glasses comprise a disordered state of matter which are structurally like liquids, but whose dynamics are characterized by extremely slow relaxation. These systems fail to relax within timescales accessible in the laboratory. At the particulate scale, many types of relaxation processes are possible that can involve an atom, a molecule, a part of molecule, a group of molecules or particles. It is important to study how these microscopic relaxation processes slow down as glass-forming materials are quenched below their glass transition temperatures, with their relaxation timescales exceeding the observation timescales as the system falls out of equilibrium.

Relaxation processes in glass formers can be classified in two categories: the primary and the secondary relaxation processes [1,2]. The former is involved with the orientational rearrangements of the constituent particles and leads to structural relaxation. Such a relaxation process, ubiquitous in molecular glasses or supercooled liquids, metallic glasses, polymer glasses and other glass formers, is generally known as the α-relaxation process [1,3]. Secondary relaxation processes, also known as β-relaxation processes, are much faster than the α-relaxation process, typically involve the motion of a molecule or a part of a molecule and are generally believed to have no connection with the glass transition process [4]. It is seen from the pioneering work by Johari and Goldstein on rigid...
molecular glass formers that the presence of a secondary relaxation is an intrinsic feature of the glassy state [5]. Later, it was demonstrated in many experimental and simulation studies that the α-relaxation process has a close relationship with a secondary relaxation process known as the Johari-Goldstein β-relaxation (J-G) process [4,6–10]. The J-G relaxation process, which is also known as “slow” secondary relaxation in the literature, is generally considered to be universal in nature as it appears in a variety of glass formers such as supercooled liquids, metallic glasses, polymeric glasses and plastic crystals. It involves all parts of a molecule or a particle and is particularly important in glassy systems because of its very close relationship with the α-relaxation process. However, the absence of any experimentally reported result involving the detection of a J-G β-relaxation mode in colloidal glasses has raised questions regarding its universality.

After decades of research, a general route is used to classify the secondary relaxation processes in glass formers based on their dynamic properties [4] and their relation to the structural relaxation process. This involves a characterization of the glass former in terms of the following criteria: i) whether the molecule possesses internal degrees of freedom; ii) the involvement of the whole molecule or part of a molecule in the secondary relaxation process; iii) the separation between $\tau_\beta$ and $\tau_\alpha$, the primary or structural relaxation times; iv) the relationship between $\tau_\beta$ and $\tau_0$, where $\tau_0$ is the independent primitive relaxation time according to the coupling model; v) the temperature dependence of the secondary relaxation strength $\Delta \tau$ (measured from dielectric spectroscopy) across the glass transition temperature $T_g$; vi) the aging behavior of $\tau_\beta$ and $\Delta \tau$ below $T_g$ and vii) the merging of $\tau_\beta$ with the primary relaxation time $\tau_\alpha$ at very high temperatures.

We study the microscopic relaxation processes for Laponite suspensions, a model soft glassy material, by dynamic light scattering (DLS) experiments. A Laponite particle is disk-shaped (diameter = 25–30 nm and thickness $\approx$ 1 nm) and belongs to the 2:1 phyllosilicates family with layered hydrous magnesium silicate. Aqueous suspensions of Laponite are known to form different phases, e.g., Wigner glass, gel, nematic phase, attractive glass etc., depending on clay concentration, ionic strength and waiting time after preparation [11]. The slowing down of the dynamics of Laponite suspensions has many similarities with the dynamic slowing-down observed in supercooled liquids [12]. Recent experimental results show the self-similar nature of the relaxation processes for different physicochemical parameters and the importance of inter-particle attractions on the relaxation dynamics in the former system [13]. In this work, we focus on the secondary relaxation process of Laponite suspensions. α- and β-relaxation timescales are estimated from the autocorrelation functions obtained in DLS measurements for Laponite suspensions with different concentrations ($C_L$), salt concentrations ($C_S$) and temperatures ($T$). We measure the primitive relaxation timescales from the α-relaxation time and the stretching exponent $\beta$ by applying the coupling model for highly correlated systems. Our experimental results suggest that the β-relaxation process involves all parts of the Laponite particle and is coupled with the primitive relaxation process. The ergodicity breaking time is seen to be correlated with the activation energy of the β-relaxation process for all $C_L$, $C_S$ and $T$. Our study indicates that the β-relaxation process of colloidal glasses of Laponite demonstrates several similarities with the J-G β-relaxation processes and may, indeed, be a J-G β-relaxation mode.

**Sample preparation and experimental methods.** – Laponite (Laponite RD®) powder is procured from BYK Additives, Inc. The powder is dried for up to 16 hours at 120°C in an oven to remove absorbed water. Dried Laponite is added to Millipore water (resistivity 18.2 MΩ-cm) and is stirred vigorously using a magnetic stirrer until the suspension appears optically clear. The suspension is filtered at a constant flow rate of 3.0 ml/min using a syringe pump (Fusion 400, Chemxy Inc.) and a 0.45 μm Millipore Milllex-HV syringe-driven filter unit. A sodium chloride (NaCl) procured from Sigma-Aldrich solution of a predetermined concentration is prepared and added using a pipette to the filtered Laponite suspensions.

Each suspension is vigorously stirred for 5–10 min. The sample is filled in a cuvette and then sealed with wax and tape for the DLS experiments. The waiting time or the aging time, $t_w$, is calculated from the moment the sample is sealed. A Brookhaven Instruments Corporation (BIC) BI-200SM spectrometer and a 532 nm solid-state laser (NdYVO₄, Coherent Inc., Spectra Physics) of output intensity 150 mW are used in the DLS experiments. The temperature $T$ of the suspension is controlled by water circulation with a temperature controller (PolyScience Digital). The intensity autocorrelation function of the scattered light, $g^{(2)}(t) = \frac{I(t) - I(0)}{I(0)} = 1 + A g^{(1)}(t)^2$, is measured using a digital autocorrelator (Brookhaven BI-9000AT) [14]. Here, $I(t)$ is the intensity of the scattered light at a delay time $t$, $g^{(1)}(t)$ is the normalized electric-field autocorrelation function and $A$ is the coherence factor. The concentration of Laponite, expressed in % w/v, refers to the weight of Laponite powder in grams that is mixed in 100 ml (100 gm) of water.

**Results and discussions.** – Intensity autocorrelation functions $g^{(2)}(t)$ are acquired in dynamic light scattering experiments as a function of the waiting time $t_w$ of aging Laponite suspensions. In fig. 1(a), we plot the normalized intensity autocorrelation function, $C(t) = g^{(2)}(t) - 1$, as a function of delay time $t$ for several waiting times for a 2.5% w/v Laponite suspension at 25 °C and at a scattering angle $\theta = 90°$. It is seen from this figure that the $C(t)$ data show two-step relaxations, with the slow relaxation process progressively slowing down with $t_w$. The two-step relaxation of $C(t)$ can be expressed as the sum of an
exponential and a stretched exponential decay [12,15,16].

\[ C(t) = [a \exp \{-t/\tau_1\} + (1 - a) \exp \{-((t/\tau_{ww})^\beta)\}]^2. \] (1)

In eq. (1), \(a\), \(\tau_1\), \(\tau_{ww}\) and \(\beta\) are the four fitting parameters corresponding to the relaxation strength, the fast relaxation time, the slow relaxation time and the stretching exponent respectively. \(C(t)\) in eq. (1) is a second-order autocorrelation function, with the two terms within the brackets giving the first-order autocorrelation function \(g^{(1)}(t)\). It is noted here that dielectric spectroscopy, which yields a first-order correlation function due to dipole-dipole correlations, has been often used to study relaxation processes of molecular glass formers [17].

We plot \(\tau_1\) and \(\langle \tau_{ww} \rangle\) vs. \(1/q^2\) in figs. 1(b) and (c), where \(q\) is the scattering wave vector at two different waiting times \((t_w = 1\ h\) and \(30\ h)\) for a 2.5\% w/v Laponite suspension. A straight line passing through the origin indicates that both the relaxation processes at 25\°C are diffusive, i.e., \(\tau_1 = 1/D_1q^2\) and \(\langle \tau_{ww} \rangle = 1/D_2q^2\), where \(D_1\) and \(D_2\) are the diffusion coefficients corresponding to the fast and slow relaxation processes respectively. Another important observation is that both \(\tau_1\) and \(\langle \tau_{ww} \rangle\) slow down with \(t_w\). The value of \(a\) in eq. (1) is always in the range 0.15–0.35. It increases with decreasing \(C_L\) and increasing \(T\), while remaining almost unchanged when \(C_S\) is changed [18].

The approach of a spontaneously evolving Laponite suspension towards a kinetically arrested state can be compared to the glass transition in molecular glasses upon rapid cooling of the latter to avoid the crystalline state. It was demonstrated in an earlier work that Arrhenius and Vogel-Fulcher-Tammann (VFT) dependences of the fast and the slow relaxation times on waiting time, respectively, are obtained if the waiting time \(t_w\) of a spontaneously evolving Laponite suspension is mapped with the inverse of the thermodynamic temperature \(1/T\) of molecular glasses [12]. Consequently, the \(t_w\)-dependence of \(\tau_1\) and \(\langle \tau_{ww} \rangle\) are given by the following equations [12]:

\[ \tau_1 = \tau_1^0 \exp \left[ \frac{t_w}{T_\alpha^0} \right]. \] (2)

and

\[ \langle \tau_{ww} \rangle = \langle \tau_{ww} \rangle^0 \exp \left[ \frac{Dt_w}{T_\alpha^0 - t_w} \right]. \] (3)

In eq. (2), the fitting parameter \(\tau_1^0 = \tau_1(t_w \to 0)\), while \(T_\alpha^0\) is the characteristic timescale associated with the slowing down of the secondary relaxation process. In eq. (3), \(D\), \(\langle \tau_{ww} \rangle^0\) and \(t_\alpha^0\) are the three fitting parameters. \(D\) is the fragility or strength parameter which quantifies the deviation from Arrhenius behavior, \(\langle \tau_{ww} \rangle^0 = \langle \tau_{ww} \rangle(t_w \to 0)\), and \(t_\alpha^0\) is the Vogel time, or the waiting time at which \(\langle \tau_{ww} \rangle \to \infty\) [12].

In fig. 2(a), the time evolution of \(\tau_1\) is plotted vs. \(t_w\) for two scattering angles (\(\theta = 60^\circ\) and \(90^\circ\)) for a 2.5\% Laponite suspension. It can be seen from fig. 2(a) that \(\tau_1\) decreases with \(t_w\) at small \(t_w\), while it increases for higher \(t_w\) for all the Laponite suspensions with different \(C_L\), \(C_S\) and \(T\) investigated here. It is known that Laponite particles can form tactoids or rigid aggregates consisting of more than one platelet in aqueous suspension [19–21]. At the early stage of dispersion, these tactoids exfoliate and the rate of exfoliation decreases with time as the intertactoid Coulombic repulsion increases rapidly with time [19]. This tactoid fragmentation process results in the speeding up of the dynamics and gives rise to the observed nonmonotonicity in the \(\tau_1\) vs. \(t_w\) plot at small \(t_w\) (fig. 2) [12]. It is seen from fig. 2 that the later increasing part of \(\tau_1\) can be fitted to eq. (2), with the rate of increase becoming higher for higher values of \(C_L\), \(C_S\) and \(T\).

The diffusion coefficient \(D_1\) of a sphere is related to its relaxation time \(\tau_1\) by the relation \(\tau_1 = 1/D_1q^2\) [14]. \(D_1\) can be estimated for a dilute suspension of monodisperse spheres from the Stokes-Einstein relation, \(D_1 = k_BT/6\pi\eta r_h\) [14], where \(k_B\), \(\eta\) and \(r_h\) are the Boltzmann constant, viscosity of the medium (0.89 mPa s at 25\°C)
and hydrodynamic radius ($r_h = d_s/2$) of the particle, respectively. It follows, therefore, that $\tau = 1/D_1 q^2 = 6\pi \eta r_h/k_B T q^2$. As the Laponite platelet is a disk-shaped particle (diameter $d = 25$–$30$ nm and thickness $h = 1$ nm approximately [22]), its equivalent spherical diameter (ESD) is given by the Jennings-Parslew relation,

$$d_s = d \left( \frac{3 \arctan(\sqrt{d/h})^2}{2 \sqrt{d/h}} \right)^{1/2}$$

[23]. Using this relation, the estimated value of $d_s$ for a Laponite platelet is $7.5$–$8.3$ nm and the estimated value of the diffusion timescale of the platelet $\tau$ is $30$–$34$ µs and $62$–$68$ µs at $q = 0.0223$ nm$^{-1}$ ($\theta = 90^\circ$) and $q = 0.0157$ nm$^{-1}$ ($\theta = 60^\circ$) respectively. It is seen from fig. 2(a) that the values of $\tau_0^\beta$, i.e. $\tau_1(t_w \to 0)$, is $34$ µs and $63$ µs for $\theta = 90^\circ$ and $\theta = 60^\circ$, respectively. Therefore, $\tau_1$ can be associated with a relaxation process that involves a single Laponite platelet.

It was an empirical observation for many supercooled liquids that the glass transition temperature $T_g$ is proportional to the activation energy $E_\beta$ of the slow secondary $\beta$-relaxation process [24,25]. We define an ergodicity breaking time $t_\beta$ for Laponite suspensions from the time evolution of $\langle t_{\beta_{ww}} \rangle$. In fig. 2(e), it can be seen that $\langle t_{\beta_{ww}} \rangle$ increases with $t_w$ for all $C_L$, $C_S$, and $T$. It can also be seen that the time evolution of $\langle t_{\beta_{ww}} \rangle$ can be fitted to eq. (3) very well. In supercooled liquids $T_g$ is defined as the temperature at which the mean $\alpha$-relaxation time is $100$ s [3]. Similarly, for the Laponite suspensions studied here, $t_\beta$ is defined as the waiting time at which $\langle t_{\beta_{ww}} \rangle = 100$ s and is extrapolated from fits to eq. (3). In fig. 2(f), the characteristic timescale $t_\beta^\infty$, associated with the fast relaxation process and extracted from fits to eq. (2) (figs. 2(b), (c) and (d)), is plotted vs. $t_\beta$ for Laponite suspensions with different $C_L$, $C_S$, and $T$. It is seen from the figure that $t_\beta^\infty \propto \tau_\beta$, with $\beta$ is defined as the temperature at which the mean $\alpha$-relaxation process is a non-exponential process and is expressed in terms of a stretched exponential function (eq. (1)). The non-exponential decay arises due to a distribution of relaxation timescales that is given by the well-known
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Fig. 3: (Colour online) (a) Stretching exponent $\beta$ vs. $\log (C_l)$ (open symbols) and $\log (\tau_{ww}/\tau_1)$ (solid symbols) for Laponite suspensions with three different $C_L$, $C_S$ and $T$ ($C_L = 2.5\%$, $C_S = 0.05 \text{ mM}$ and $T = 25^\circ\text{C}$ ($\square$); $C_L = 3.0\%$, $C_S = 0.05 \text{ mM}$ and $T = 25^\circ\text{C}$ ($\bullet$) and $C_L = 3.0\%$, $C_S = 0.5 \text{ mM}$ and $T = 25^\circ\text{C}$ ($\triangle$)). (b) $\log (\tau_1)$ ($\square$) and $\log (\tau_{ww})$ ($\bullet$) of Laponite suspensions of $t_w = 5.5 \text{ h}$ vs. $C_L$ ($C_S = 0.05 \text{ mM}$ and $T = 25^\circ\text{C}$).

Kohlrausch-Williams-Watts distribution: $P_{ww}(\tau) = -\frac{(-1)^k}{\pi^2} \sin(\pi \beta k) \Gamma(\beta k + 1) (\frac{\tau}{\tau_{ww}})^{\beta k + 1}$ [27]. The width $w$ of the distribution is related to the stretching exponent $\beta$ by $w = \frac{\tau_{ww}}{\tau_1} - 1 = \frac{\beta^2(2\beta)}{\Gamma(4/\beta)} - 1$. In fig. 3(a), we plot $\beta$ vs. $\log (\tau_1)$ and $\log (\tau_{ww}/\tau_1)$, indicating that the width of the $\alpha$-relaxation process is indeed coupled with the secondary relaxation time [6–9,26]. Furthermore, the superposition of $\beta$ values for all $C_L$, $C_S$ and $T$ when plotted vs. $\log (\tau_1)$ and $\log (\tau_{ww}/\tau_1)$ is reminiscent of the self-similarity of the relaxation processes $\tau_1$ and $\langle \tau_{ww} \rangle$ with changes in $C_L$, $C_S$ and $T$ [13].

It was observed from dielectric measurements that the separation between the $\alpha$ and $\beta$ relaxation peaks is greater at elevated pressures for molecular glass formers, thus confirming the sensitivity of the $\beta$-relaxation process to high pressures [28]. In fig. 3(b), we plot $\log (\tau_1)$ and $\log (\tau_{ww})$ for different $C_L$ for a fixed waiting time $t_w = 5.5 \text{ h}$. It is seen from this figure that both $\tau_1$ and $\tau_{ww}$ increase with $C_L$. Since increasing $C_L$ is analogous to increasing pressure on the system as a larger number of particles are packed in a fixed volume, both the relaxation processes of Laponite suspensions are clearly sensitive to changes in pressure or concentration.

It is observed in a variety of glass formers that the order of magnitude of the $\text{J-G}$ $\beta$-relaxation time $\tau_\beta$ lies very close to the primitive $\alpha$-relaxation time $\tau^*$ of the coupling model [4,6,7,28–31]. According to the coupling model, the relaxation process of a complex system depends on the interactions among the relaxation units. A relaxation unit relaxes independently with a rate $W_0 = 1/\tau_0$ at a time $t$ that is shorter than a crossover or characteristic time $\tau_c$. The correlation function $\phi(t)$ can be expressed by a simple exponential function, $\phi(t) = \exp(-t/\tau_0)$. For Laponite suspensions, $\phi(t)$ is the first order or the electric-field autocorrelation function and can be measured in DLS experiments. At longer times, i.e. $t > \tau_c$, the primitive relaxation rate slows down and becomes time-dependent due to the many-body interactions or the coupling between relaxation units and can be expressed by $W(t) = W_0(t/\tau_c)\sim W_0(t/\tau_c)^{\beta-1}$, where $n = 1 - \beta$ is the coupling parameter and $\beta$ is the stretching exponent in eq. (1). It is observed that $\tau_c$ is insensitive to the temperature of a molecular glass former. In the regime $t > \tau_c$, the correlation function can be described by a stretched exponential function $\phi(t) = \exp[-(t/\tau^*)^\beta]$, where $\tau^*$ is the effective relaxation time and is related to $\tau_0$ (or $W_0^{-1}$), the initial primitive relaxation time in the absence of coupling, by the following expression:

$$\tau^* = \left[\beta \tau_0^{\beta-1} W_0^{-1}\right]^{1/\beta} \cdot \quad (4)$$

In the absence of coupling at short times $t < \tau_c$, the relaxation process is unaffected by many-body dynamics and the system relaxes with a relaxation time $\tau_0$. However, many-body coupling at long times $t > \tau_c$ leads to a fractional decay of $\phi(t)$ with stretched exponential relaxation [7,32]. The microscopic relaxation rate $W_0$ is related to the diffusion coefficient $D_0$ of a single relaxation unit by $W_0 = (D_0 q^2)$ with $D_0 = d_s^2/\tau_0$. Therefore, eq. (4) can be written in the following form [33]:

$$\tau^* = \left[\beta \tau_0^{\beta-1} \frac{\tau_0}{D_0 q^2}\right]^{1/\beta} \cdot \quad (5)$$

It was reported in an earlier work that $\tau_c$ is concentration dependent for Laponite suspensions and that its value at higher concentrations ($C_L > 1.5\% \text{ w/v}$) is approximately 20 $\mu$s [32]. Remarkably, the estimated value of the primitive relaxation time $\tau_0$ (i.e., $t < \tau_c$) from eq. (5) ($d_s = 7.5 \text{ nm}$, $q = 0.0223 \text{ nm}^{-1}$, $\beta = 0.329$, $\tau^* = \tau_{ww} = 49670 \mu$s) is approximately 22 $\mu$s, which is of the same order of magnitude as $\tau_1$ (fig. 2). This result closely resembles the observation in molecular glass formers where the primitive and the $\text{J-G}$ $\beta$-relaxation times are of the same order of magnitude. These observations indicate that the $\beta$-relaxation process of Laponite suspensions is a plausible candidate for the $\text{J-G}$ $\beta$-relaxation process [29–31].

Conclusions. In this work, we have extracted the primary and secondary relaxation timescales of Laponite suspensions with different Laponite concentrations ($C_L$), salt concentrations ($C_S$) and temperatures ($T$) from intensity autocorrelation functions obtained from dynamic light
scattering (DLS) measurements. A well-known route is followed to characterize the secondary relaxation timescales that are extracted from our experiments [4]. It is observed that the secondary relaxation process of aging Laponite suspensions involves a single rigid Laponite particle. Furthermore, it is coupled with the primary relaxation process as its ergodicity breaking time $t_g \propto t_\alpha^2$, the characteristic timescale associated with the $\beta$-relaxation process. It is also demonstrated that the width $w$ of the distribution of the $\alpha$-relaxation timescale is correlated with the $\beta$-relaxation time. Both $\tau_1$ and $\tau_{\text{ww}}$ are found to be very sensitive to a concentration within the range of $C_L$ explored here. Finally, it is observed that the order of magnitude of the primitive relaxation time $\tau_0$, estimated from the coupling model, is the same as that of the secondary $\beta$-relaxation time $\tau_1$. Our experimental observations therefore clearly suggest that the $\beta$-relaxation process of a colloidal Laponite glass shows many characteristics of the J-G $\beta$-relaxation process reported for molecular glass formers. Interestingly, the size of the Laponite particle (ESD $\approx 8 \text{ nm}$) is only a little bigger than a molecule ($0.1 \text{ nm} < \text{ ESD} < 1 \text{ nm}$). Laponite particles are asymmetric in shape, have charge anisotropy and are often categorized as patchy particles. Similarly, a molecule, which is the building block for a molecular glass former, is asymmetric and possesses non-uniform charge distribution. Colloidal patchy particles of Laponite form colloidal glasses at very low concentrations (volume fraction $< 0.02$), which allows adequate volume for the whole particle to reorient and diffuse and to take part in the relaxation processes. Clearly, these factors have contributed to making glassy Laponite suspensions a leading candidate among several well-known colloidal glass formers to exhibit the J-G $\beta$-relaxation mode.

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