

Kinetics of the glass transition of fragile soft colloidal suspensions

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Microscopic relaxation time scales are estimated from the autocorrelation functions obtained by dynamic light scattering experiments for Laponite suspensions with different concentrations (C_L), added salt concentrations (C_S), and temperatures (T). It has been shown in an earlier work [D. Saha, Y. M. Joshi, and R. Bandyopadhyay, *Soft Matter* **10**, 3292 (2014)] that the evolutions of relaxation time scales of colloidal glasses can be compared with molecular glass formers by mapping the waiting time (t_w) of the former with the inverse of thermodynamic temperature ($1/T$) of the latter. In this work, the fragility parameter D , which signifies the deviation from Arrhenius behavior, is obtained from fits to the time evolutions of the structural relaxation time scales. For the Laponite suspensions studied in this work, D is seen to be independent of C_L and C_S but is weakly dependent on T . Interestingly, the behavior of D corroborates the behavior of fragility in molecular glass formers with respect to equivalent variables. Furthermore, the stretching exponent β , which quantifies the width w of the spectrum of structural relaxation time scales, is seen to depend on t_w . A hypothetical Kauzmann time t_k , analogous to the Kauzmann temperature for molecular glasses, is defined as the time scale at which w diverges. Corresponding to the Vogel temperature defined for molecular glasses, a hypothetical Vogel time t_α^∞ is also defined as the time at which the structural relaxation time diverges. Interestingly, a correlation is observed between t_k and t_α^∞ , which is remarkably similar to that known for fragile molecular glass formers. A coupling model that accounts for the t_w -dependence of the stretching exponent is used to analyse and explain the observed correlation between t_k and t_α^∞ . © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4936625>]

I. INTRODUCTION

The dependence of transport properties (diffusivity, viscosity, etc.) and structural relaxation times near the glass transition are of crucial importance in understanding glass formers. A few key observations, like the rapid increase of viscosity near the glass transition temperature T_g , the heat-capacity jump at T_g , the Kauzmann entropy catastrophe, the super-Arrhenius temperature dependence of the structural relaxation processes, and fragile behavior, are common to many glass formers.^{1–3} An enormous increase in viscosity and relaxation time (14 decades and more) is observed as a molecular glass former is quenched towards its glass transition temperature.⁴ Specific heat measurements show a jump in the heat-capacity at T_g and the extent of the jump, in general, is larger for a fragile glass.² Fragile glasses show super-Arrhenius temperature dependence and exhibit an extremely steep increase in viscosity η , which can be expressed by the Vogel-Fulcher-Tammann (VFT) relation, i.e., $\eta = \eta_0 \exp [DT_0/(T - T_0)]$. Here, T_0 is the Vogel temperature at which η diverges. The fragility parameter D quantifies the deviation from Arrhenius behavior. D is a material specific quantity,⁵ whose magnitude is small (typically <10) for fragile supercooled liquids and can change to very large

values for strong glass formers. It is very difficult to differentiate between an Arrhenius temperature dependence and a super-Arrhenius temperature dependence^{5,6} for $D > 100$.

The relation between the fragility parameter D and the structural properties of a material is still not completely understood despite many theoretical and experimental studies. A correlation is drawn between the fragility of a material and its physical properties, i.e., its Poisson's ratio or the relative strength of its shear and bulk moduli.⁷ The relation between the nature of the interaction potential and fragility has also been studied for model binary mixture glass formers⁸ and colloidal glass formers.⁹ In the supercooled liquids literature, T_g is the temperature at which the mean α -relaxation time ($\langle\tau_\alpha\rangle$) is 100 s.^{5,6} It is to be noted that T_g depends on the heating or cooling rate.¹⁰

The phenomenology of glass formers has often been described by a potential energy landscape (PEL),^{11,12} which can be visualized in terms of a multi-dimensional surface describing the dependence of the potential energy of the system as a function of the particle coordinates.¹³ If N is the number of particles, then the dimension of the hyperspace is $3N + 1$, with the system represented by a point evolving temporally in this complex potential hyperspace.¹³ In this topographic description, the minima of the PEL correspond to mechanically stable arrangement of particles.¹³ A correlation is drawn between the fragility of a glass former and the density of minima in the PEL. Fragile glass formers are observed to have more density of minima than strong

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glass formers.⁵ Interestingly, the PEL is particularly useful to calculate another important quantity, the configurational entropy (S_c) of a supercooled liquid.¹⁴ In the supercooled regime, S_c is the excess entropy of the liquid over its crystalline phase. At a hypothetical temperature known as Kauzmann temperature T_K , S_c vanishes and the system is postulated to go through a thermodynamic transition to avoid a catastrophe (the Kauzmann catastrophe), which would require the entropy of the crystalline state to be greater than that of the liquid state. The resultant “ideal glass” state corresponds to the global minimum of the PEL.¹¹

Even after decades of research, a proper understanding of the ideal glass state and the link between the thermodynamics and kinetics of glass formers remain elusive. However, it is seen that for most fragile supercooled liquids, T_K is approximately equal to T_0 , indicating a possible relation between its thermodynamics and kinetics.⁶ The random first order transition theory of the glass transition predicts a possible relation between the stretching exponent β of the non-Debye α -relaxation and T_K .¹⁵ It is believed that β is temperature dependent and vanishes at T_K which corresponds to the divergence of the width w of the α -relaxation spectrum.^{15,16}

In this work, we have carried out detailed experimental measurements of the microscopic relaxation time scales of colloidal suspensions of Laponite approaching the jamming transition by dynamic light scattering experiments. The evolutions of microscopic relaxation time scales are studied for Laponite suspensions with different concentrations (C_L), added salt concentrations (C_S), and temperatures (T). It is seen that the evolutions of relaxation time scales of Laponite for all C_L , C_S , and T can be compared with molecular glass formers if the waiting time (t_w) of the former is mapped with the inverse of thermodynamic temperature ($1/T$) of the latter.¹⁷ We also report the effects of these variables on the fragility parameter D and Vogel time t_α^∞ and compare these findings with the results reported for the molecular glass formers. The stretching exponent β , associated with non-Debye structural relaxation processes, is also extracted for different waiting times t_w for samples of different C_L , C_S , and T . A hypothetical time scale t_k at which the width of the distribution of structural relaxation times diverges is defined by extrapolating $\beta \rightarrow 0$. It is shown here that this time scale is correlated to the time scale t_α^∞ at which the mean structural relaxation time diverges. This remarkable correlation between these two hypothetical time scales is reminiscent of the correlation of two hypothetical temperatures, Kauzmann and Vogel temperatures, seen previously in extremely fragile molecular glass formers. We explain this correlation by appropriately modifying the coupling model proposed for molecular glass formers and by analyzing the observed waiting time dependence of β associated with the primary relaxation process of Laponite particles in suspension.

II. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

Laponite RD® (BYK, Inc.) is dried in an oven for more than 16 h to remove the absorbed water. A homogeneous

and optically clear aqueous suspension is prepared by vigorous mixing of Laponite with Millipore water (resistivity 18.2 MΩ-cm) and subsequent filtration at a constant flow rate (3.0 ml/min) by a syringe pump (Fusion 400, Chemyx, Inc.). Salt concentration is adjusted by precise addition of a concentrated solution of NaCl (Sigma-Aldrich) of a known molarity by a pipette under vigorous mixing. Next, the Laponite suspension is sealed immediately in a cuvette. Aging time or waiting time t_w is calculated from the moment the sample is sealed. DLS experiments are performed by a Brookhaven Instruments Corporation BI-200SM spectrometer equipped with a temperature controller (Polyscience Digital). Details of the set-up are given elsewhere.¹⁷ The normalized intensity autocorrelation function of the scattered light, $g^{(2)}(q, t) = \frac{\langle I(q, 0)I(q, t) \rangle}{\langle I(q, 0) \rangle^2} = 1 + A|g^{(1)}(q, t)|^2$, is obtained as a function of delay time t from a digital autocorrelator (Brookhaven BI-9000AT), where $I(q, t)$ is the intensity of the scattered light at a delay time t for wavevector $q = 0.022 \text{ nm}^{-1}$ (i.e., $q = 4\pi n/\lambda \sin(\theta/2)$). This corresponds to a scattering angle $\theta = 90^\circ$ and a length scale $1/q = 45 \text{ nm}$ approximately. Finally, $n = 1.334$ is the refractive index of the medium and $\lambda = 532 \text{ nm}$ is the wavelength of the laser. $g^{(1)}(q, t)$ and A are the normalized electric field autocorrelation function and the coherence factor, respectively.¹⁸

III. RESULTS AND DISCUSSIONS

Intensity autocorrelation functions $g^{(2)}(t)$ are obtained as a function of the waiting time t_w . In Figure 1(a), the normalized intensity autocorrelation function, $C(t) = g^{(2)}(t) - 1$, for a 2.5% w/v Laponite suspension with 0.05 mM salt at 25 °C, is plotted as a function of delay time t for several t_w values. Two-step relaxation processes, which become more prominent as t_w increases, are observed in $C(t)$. It is also seen that the decay of $C(t)$ slows down with t_w and can be expressed by a sum of an exponential and a stretched exponential decay in the following way:^{17,19,20}

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

The data in Figure 1(a) are fitted to Equation (1), with τ_1 , τ_{ww} , a , and β being the fitting parameters. The fast decay is expressed by an exponential function and describes a relaxation time quantified by a time scale τ_1 , the fast relaxation time. Similarly, the slow decay is represented by a stretched exponential function, where τ_{ww} and β are the slow relaxation time and stretching exponent respectively.¹⁹ The mean slow relaxation time is given by Ref. 21 $\langle \tau_{ww} \rangle = (\tau_{ww}/\beta)\Gamma(1/\beta)$. In figures 1(b) and 1(c), τ_1 and $\langle \tau_{ww} \rangle$ are plotted vs. $1/q^2$. Linear fits passing through the origin confirm the diffusive natures of both relaxation processes.

Response functions characterised by two-step decays are ubiquitous in glass formers.^{22–24} In supercooled liquids and in the present system, the faster decay involves diffusion of a particle within a cage formed by its neighbours,²⁵ while the slower decay (α -relaxation process) is connected to structural or orientational rearrangements.⁶ The mean slow relaxation time $\langle \tau \rangle$ is very sensitive to changes in temperature and can be expressed by the Vogel-Fulcher-Tammann relation⁶ $\langle \tau \rangle = \tau_{VF} \exp[B/(T - T_0)]$, where the

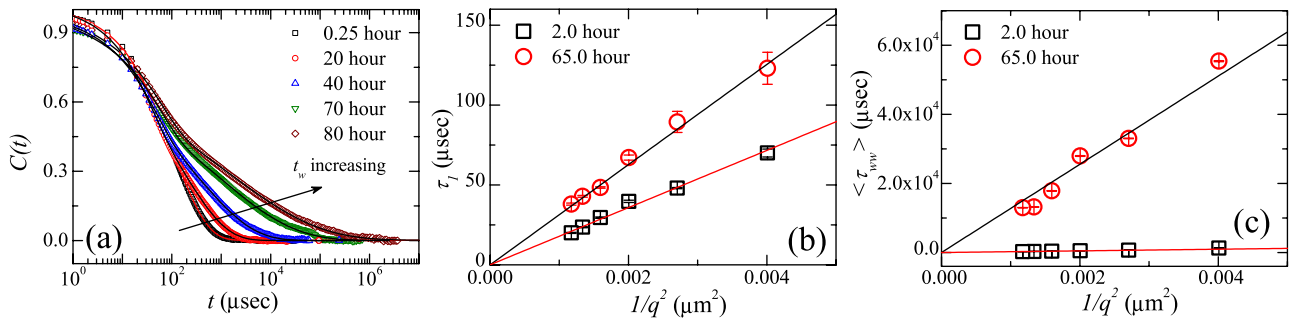


FIG. 1. (a) The normalized intensity autocorrelation functions $C(t)$, vs. the delay time t , at 25 °C and scattering angle $\theta = 90^\circ$, for 2.5% w/v Laponite suspension with 0.05 mM salt at several t_w . The solid lines are fits to Equation (1). The diffusive behavior of the fast relaxation time (τ_1) and the mean slow relaxation time ($\langle\tau_{ww}\rangle$) are shown in (b) and (c), respectively, for a 2.5% w/v Laponite suspension. The solid lines are linear fits passing through the origin.

fitting parameter $\tau_{VF} = \langle\tau\rangle(T \rightarrow \infty)$. B and T_0 are identified as the fragility index and the Vogel temperature, respectively. For quantifying the deviation from Arrhenius behavior, i.e., $\langle\tau\rangle = \tau \exp(E/k_B T)$, one can define $B = DT_0$, where D is the strength or fragility parameter.^{2,5,6} As discussed earlier in the introduction, the slowing down of the relaxation processes in Laponite suspension can be compared to the dynamics of supercooled liquids by performing a one-to-one mapping between the waiting time t_w of a spontaneously evolving Laponite suspension and the inverse of the temperature $1/T$ of a supercooled liquid that is quenched towards the glass transition.¹⁷ The mapping works well as the reduction in mobility with decrease in temperature in fragile molecular glass formers is analogous to the decrease in particulate mobility in Laponite suspensions with increase in waiting time. It was also reported that τ_1 increases exponentially with t_w , i.e., $\tau_1 = \tau_1^0 \exp(t_w/t_\beta^\infty)$, where t_β^∞ is the characteristic time associated with the slowdown of the fast relaxation process. Simultaneously, $\langle\tau_{ww}\rangle$ shows a VFT-type dependence on t_w given by the following

expression:¹⁷

$$\langle\tau_{ww}\rangle = \langle\tau_{ww}\rangle^0 \exp(Dt_w/(t_\alpha^\infty - t_w)). \quad (2)$$

In Equation (2), D is the fragility parameter discussed earlier and t_α^∞ is identified with the Vogel time or the waiting time at which $\langle\tau_{ww}\rangle$ diverges.

In Figure 2(a), $\langle\tau_{ww}\rangle$ values extracted from fits of the autocorrelation data to Equation (1) and the corresponding fits to Equation (2) are plotted for different values of C_L with $C_S = 0.05$ mM and $T = 25^\circ\text{C}$. It is seen from the plots that the evolution of $\langle\tau_{ww}\rangle$ becomes faster with increase in C_L .²⁶ The fragility parameters D (\bullet) and the Vogel times t_α^∞ (\square) obtained from the fits are plotted in Figure 2(b). Recent simulation results suggest that the kinetic fragility K_{VFT} ($K_{VFT} = 1/D$), calculated from the α -relaxation time for Kob-Anderson (KA) model glass formers, has a very weak dependence on density.²⁷ In the Laponite suspensions studied here, the suspension density changed from 1020 Kg m⁻³ to 1035 Kg m⁻³ when C_L is varied between 2.0% w/v and 3.5% w/v. Since the

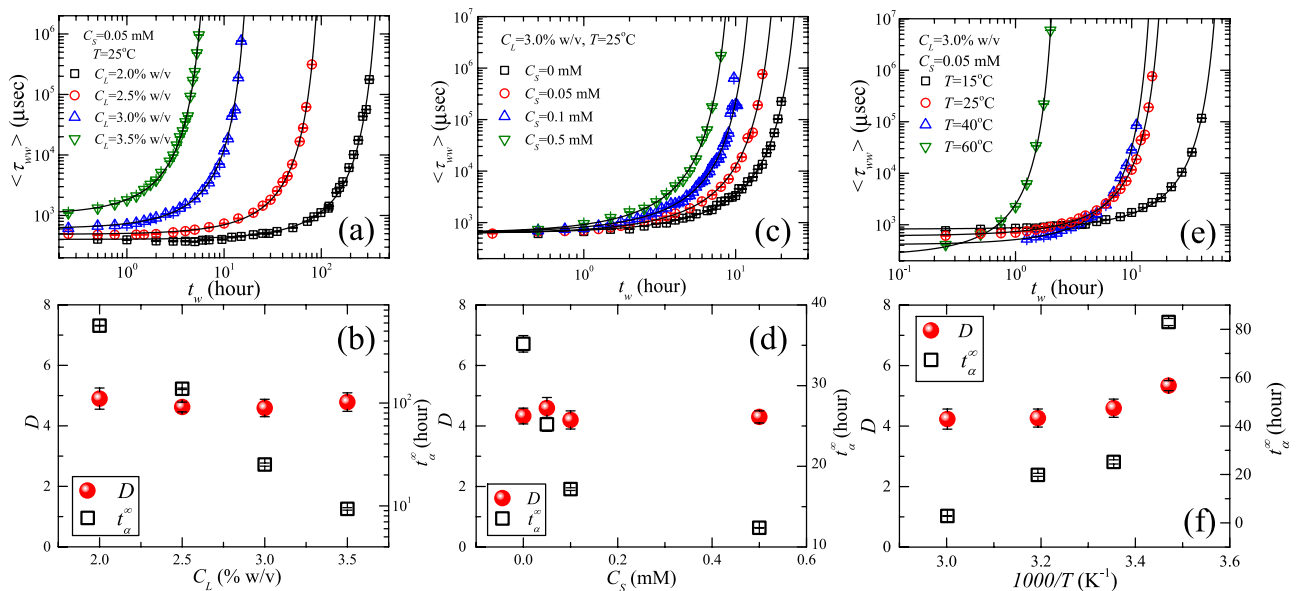


FIG. 2. Mean slow relaxation times $\langle\tau_{ww}\rangle$, obtained by fitting $C(t)$ data to Equation (1), are plotted vs. t_w for different C_L , C_S , and T in (a), (c), and (e), respectively. Fragility D (\bullet) and Vogel time t_α^∞ (\square), measured by fitting $\langle\tau_{ww}\rangle$ data to the Equation (2), are plotted for different C_L , C_S and T in (b), (d), and (f), respectively.

change in the density of Laponite suspensions studied here is very small, D can be expected to be constant. Remarkably, our experimental observation, demonstrated in Figure 2(b), supports this observation for molecular glass formers.

It is to be noted that although the bulk suspension density does not change appreciably within the range of C_L studied here, the number density of particles increases with C_L . The subsequent decrease in the interparticle distance in Laponite suspensions for higher C_L therefore translates to an increase in pressure, with more particles packing within the fixed sample volume. The apparent independence of D on number density in the Laponite suspensions studied here is reminiscent of recent results for many molecular glass formers whose isochoric fragility is independent of pressure.²⁸ It is seen from Figure 2(b) that t_α^∞ decreases monotonically with C_L . This indicates faster approach to an arrested state with increasing Laponite concentration. Since the number density of Laponite particles in suspension is directly proportional to C_L , multi-body interactions are enhanced with increasing C_L , thereby shifting the onset of the nonergodic transition to earlier times (Figure 2(a)). This feature is reminiscent of previous observations in dense colloidal suspensions^{29,30} and in the context of aging Laponite suspensions.^{17,26}

In Figure 2(c), $\langle\tau_{ww}\rangle$ is plotted for different values of C_S with $C_L = 3.0\%$ w/v and $T = 25^\circ\text{C}$.²⁶ D (\bullet) and t_α^∞ (\square) are obtained from the fits of the data to Equation (2) and are plotted in Figure 2(d). D is almost constant for the entire range of salt concentrations C_S . DLVO (Derjaguin-Landau-Verwey-Overbeek) analysis for Laponite suspensions reported earlier has revealed that the height of the repulsive barrier increases and the width of the barrier decreases with increase in C_S .²⁶ This is due to the enhancement of the screening of the interparticle repulsive interactions and the increasingly important role that interparticle attractions play in spontaneously evolving Laponite suspensions. The addition of salt and the development of interparticle attractions increase the rate of structure formation. This is verified in Figure 2(d), where t_α^∞ is seen to decrease rapidly with increase in C_S .²⁶ This corroborates our earlier observation²⁶ that the arrested state is approached at a faster rate due to stronger interparticle interactions when the concentration of salt in the system is enhanced. However, an almost constant value of D (Figure 2(d)) with increasing C_S indicates that fragility is independent of the screening effects on the interparticle interaction within the range of salt concentrations studied here.

Simulation results for binary mixtures of soft spheres have shown that fragility is independent of the softness of the repulsive interaction.³¹ However, recent computer simulation results on binary mixture glass formers with a modified Lennard-Jones type potential show that the kinetic fragility increases with increasing softness.⁸ Experiments on soft colloidal systems show that soft (more compressible) particles form stronger glasses than hard (less compressible) colloidal particles.⁹ In our experiment, it is to be noted that while the proportion of attractive and repulsive interaction changes with C_S , the softness of interparticle interactions and the compressibility of the Laponite particles do not change. This is established from the observed self-similarity

of the potential energy landscape with C_S reported earlier.²⁶ Hence, the apparent insensitivity of D to changes in C_S confirms several earlier simulations and experimental results on colloidal and molecular glass formers.^{8,9,31}

Temperature has a strong effect on the evolution of relaxation processes in Laponite suspensions.^{26,32} $\langle\tau_{ww}\rangle$ is plotted for different values of T with $C_L = 3.0\%$ w/v and $C_S = 0.05$ mM in Figure 2(e). It is seen that increase in T accelerates the time-evolution of $\langle\tau_{ww}\rangle$.^{26,32} In Figure 2(f), D (\bullet) and t_α^∞ (\square) are plotted for the data shown in Figure 2(e). It is seen that D is weakly dependent on temperature and increases by a small amount as T decreases. t_α^∞ increases with decrease in temperature, thereby indicating that the nonergodic transition is achieved at earlier times with increase in T . Increase in T is therefore equivalent to increasing the apparent cooling rate q' , with the system being driven towards the nonergodic transition at faster rates at higher temperatures. For bulk metallic glass formers, i.e., $\text{Zr}_{57}\text{Cu}_{15.4}\text{Ni}_{12.6}\text{Al}_{10}\text{Nb}_5$ and $\text{Zr}_{58.5}\text{Cu}_{15.6}\text{Ni}_{12.8}\text{Al}_{10.3}\text{Nb}_{2.8}$, there is an apparent increase in D at slower cooling rates,³³ while the Vogel temperature T_0 increases with cooling rate. The small increase in D with $1000/T$ at the slowest cooling rate (Figure 2(f)) is reminiscent of observations in molecular glass formers.³³ Given the inverse relation between T_0 and t_α^∞ (i.e., $T_0 \leftrightarrow 1/t_\alpha^\infty$),¹⁷ the decrease of t_α^∞ with increase in T or q' is also remarkably consistent with the behaviour of metallic glass formers.³³

It is seen that strong glass formers have a lower density of minima in the potential energy landscape compared to fragile glass formers.⁵ At present, the very small changes in D reported in Figure 2 indicate that the underlying energy landscapes are self-similar for the ranges of C_L , C_S , and T studied here. This is in agreement with the conclusion from very recent experimental observations that time-evolutions of the microscopic relaxation time scales and the stretching exponents β associated with the slow relaxation process show comprehensive Laponite concentration-salt concentration-temperature-waiting time superpositions, thereby indicating the self-similarity of the energy landscapes.²⁶

In Figure 3, the stretching exponent β , obtained by fitting the $C(t)$ data to Equation (1), is plotted vs. t_w for different C_L , C_S and T . It is seen that for all C_L , C_S and T , β decreases linearly with t_w . For many supercooled liquids, β depends on temperature and decreases linearly with $1/T$.¹⁶ As discussed earlier, a non-Arrhenius stretched exponential decay of the $C(t)$ data can arise due to the well-known Kohlrausch-Williams-Watts distribution of the slow relaxation time scales given by $\rho_{ww}(\tau) = \frac{\tau_{ww}}{\pi\tau^2} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \sin(\pi\beta k) \Gamma(\beta k + 1) \left(\frac{\tau}{\tau_{ww}}\right)^{\beta k + 1}$.²¹ The width w of the distribution can be written as $w = \frac{\langle\tau_{ww}^2\rangle}{\langle\tau_{ww}\rangle^2} - 1 = \frac{\beta\Gamma(2/\beta)}{(\Gamma(1/\beta))^2} - 1$. Here $\beta \leq 1$, with a lower value of β indicating a broader distribution of relaxation time scales with the width w of the distribution $\rho_{ww}(\tau)$ diverging at $\beta \rightarrow 0$.²¹ We define a time t_k as the waiting time at which $\beta \rightarrow 0$. This definition of a hypothetical divergence time t_k is similar to the definition of the Kauzmann temperature T_K for molecular glass formers where it is seen that w diverges with a vanishing β at T_K .^{15,16,34,35} From the data plotted in Figure 3, t_k is measured by extrapolating β to 0 for different C_L , C_S , and T . It is seen from the insets of Figures 3(a)-3(c)

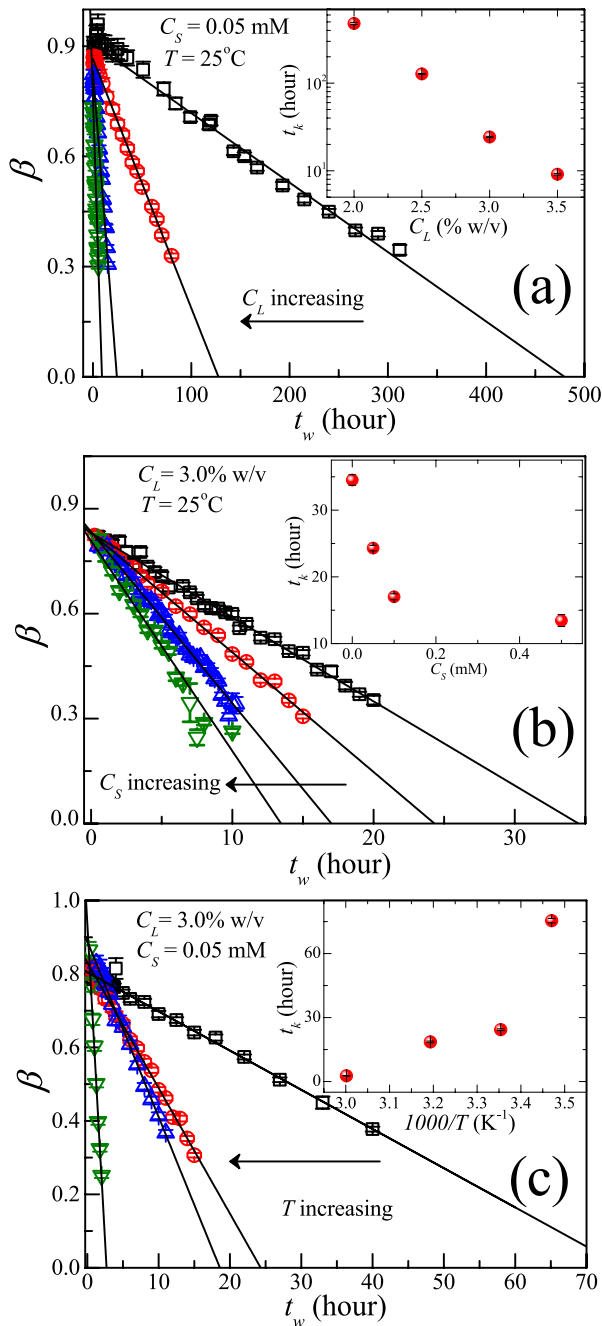


FIG. 3. (a) Stretching exponents β are plotted vs. t_w for $C_S = 0.05$ mM and $T = 25^\circ\text{C}$ at different C_L (from right to left, 2.0% w/v (\square), 2.5% w/v (\circ), 3.0% w/v (\triangle), 3.5% w/v (∇)). (b) β vs. t_w for $C_L = 3.0\%$ w/v and $T = 25^\circ\text{C}$ at different C_S (from right to left, 0 mM (\square), 0.05 mM (\circ), 0.1 mM (\triangle), 0.5 mM (∇)). (c) β vs. t_w for $C_L = 3.0\%$ w/v and $C_S = 0.05$ mM at different T (from right to left, 15°C (\square), 25°C (\circ), 40°C (\triangle), 60°C (∇)). t_k (\bullet), the waiting times at which $\beta \rightarrow 0$, measured by extrapolating of β to 0, are plotted for different C_L , C_S , and T in the insets of (a), (b), and (c), respectively.

that the extrapolated values of t_k decrease with the increase of C_L , C_S , and T .

The temperature T_K corresponding to a vanishing β in fragile supercooled liquids,^{34,35} typically calculated from the extrapolation of the temperature dependent β data, is seen to be correlated to T_0 ,^{15,16} i.e., $T_0 \approx T_K$. It is true that the deep landscape minima or traps are diverse^{11,13} and the pathways of configuration space that connect these diverse traps may result

in a broad spectrum of relaxation times leading to a very small value of β in the stretched relaxation function.¹¹ Given many similarities between supercooled liquids and aging Laponite suspensions, it is interesting to investigate if estimates of t_k for the latter have any connection with t_α^∞ , the analogous Vogel time. In Figure 4, we plot t_α^∞ vs. t_k . Remarkably, it is seen that t_k is correlated with t_α^∞ , i.e., $t_\alpha^\infty \approx t_k$ and that $4 \leq D \leq 5.5$ (inset of Figure 4) for the samples studied here. It is to be noted that values of D for sorbitol, toluene, *o*-terphenyl, propylene carbonate, triphenyl phosphite, and sucrose are 8.6, 5.6, 5.0, 2.9, 2.9, and 0.154, respectively.^{3,36} The values of D obtained for Laponite suspensions therefore compare very well with the D -values of fragile molecular glass formers, thereby confirming that Laponite suspensions are excellent candidates for the study of the nonergodic transition.³⁷

In the supercooled liquids literature, the Kauzmann temperature T_K is also known as the equilibrium glass transition temperature.³⁸ According to this theory, the system in the supercooled regime relaxes by exploring possible configurations available in the energy landscape via activated processes. A good measure of the number of available configurations at a particular temperature can be obtained by calculating the configurational entropy at that temperature and is given by $S_c(T) = S_{\text{liquid}}(T) - S_{\text{crystal}}(T)$, where S_{liquid} is the entropy of the liquid and S_{crystal} is the entropy of the crystalline state, with $S_c(T)$ vanishing as $T \rightarrow T_K$. However, it is not completely clear that a simple relation between the kinetics and the thermodynamics of a glass former (i.e., $T_0 \approx T_K$) always exists, as a systematic increase of T_k/T_0 from unity was observed for increasing values of D .³⁶ It was reported in an earlier work that the ratio T_k/T_0 lies between 0.9 to 1.2 for $D < 20$.³⁶ We plot the ratio t_α^∞/t_k vs. D for data acquired for all the Laponite suspensions of different C_L , C_S , and T studied here in the inset of Figure 4. It is seen that $0.9 \leq t_\alpha^\infty/t_k \leq 1.2$. Indeed, it was shown in an earlier study that T_K/T_0 , the ratio of the Kauzmann and Vogel temperatures, starts increasing from unity for fragile glass formers and attains higher values for strong supercooled liquids.³⁶ Although there is an apparent similarity between the results plotted in Figure 4 and T_k/T_0 ratios reported earlier,³⁶ we note that t_k is the time at which

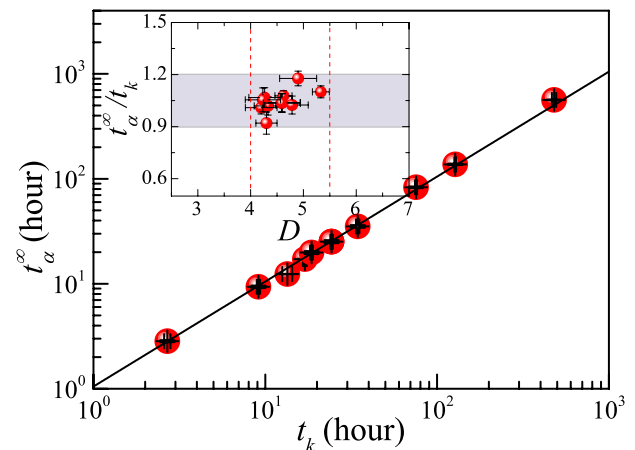


FIG. 4. Analogous Vogel time t_α^∞ is plotted vs. t_k , the waiting time at which $\beta \rightarrow 0$. Solid line is the linear fit with a slope 1.02 ± 0.025 . In the inset, the ratio t_α^∞/t_k is plotted vs. D .

$w \rightarrow \infty$ and that for the colloidal Laponite suspensions studied here, t_k has a very different physical origin compared to T_K in supercooled liquids.

We now explain the simultaneous divergence of the two hypothetical times, t_α^∞ and t_k , in terms of the Vogel-Fulcher behavior of the relaxation times and the stretched-exponential nature of the slow relaxation process.³⁹ The observed stretched exponential time dependence of the slow relaxation process can be rewritten for aging colloidal suspensions as

$$\exp\left\{-\left(t/\tau\right)^{\beta(t_w)}\right\} = \exp\left\{-t/L(t_w, t)\right\}. \quad (3)$$

Here, $L(t_w, t)$ can be interpreted as the time-dependent relaxation time and has a similar physical origin as that for supercooled liquids.³⁹ Following the coupling model proposed by Ngai *et al.*,⁴⁰⁻⁴² we relate $L(t_w, t)$ to the time-dependent relaxation rate $W(t)$ by $W(t) = \beta/L(t_w, t)$.⁴³ This model of relaxation indicates that each relaxation unit of the system relaxes independently with a primitive rate W_0 at time scales that are short when compared to the characteristic time scale $t_0 = 1/\omega_c$ associated with the coupling of the relaxing molecular units. At longer times, i.e., $\omega_c t > 1$, the primitive relaxation rate slows down and can be expressed as, $W(t) = W_0(\omega_c t)^{-n}$, $0 < n < 1$ and $n = (1 - \beta)$.⁴³ If $L(t_w, t) = L_0(t_w)(t/t_0)^{1-\beta}$,³⁹ where $L_0 = \beta/W_0$,⁴³ it follows from Equation (3) that

$$\begin{aligned} \exp\left[-\left(t/\tau\right)^\beta\right] &= \exp\left[-\frac{t}{L_0(t_w)(t/t_0)^{1-\beta}}\right] \\ &= \exp\left[-\left(\frac{t}{t_0[L_0(t_w)/t_0]^{1/\beta}}\right)^\beta\right]. \end{aligned} \quad (4)$$

Hence, τ can be rewritten as $\tau = t_0[L_0(t_w)/t_0]^{1/\beta}$.³⁹ For colloidal suspensions of Laponite, the secondary relaxation process is related to the microscopic motion of a single relaxation unit (a Laponite particle) and has the following Arrhenius dependence on t_w as discussed earlier:¹⁷ $\tau_1 = \tau_1^0 \exp(t_w/t_\beta^\infty)$. As $L_0(t_w)$ is related to the single relaxation unit,⁴³ we assume an Arrhenius dependence of $L_0(t_w)$ on t_w for colloidal suspension of Laponite, $L_0(t_w) = L \exp(t_w/t_\beta^\infty)$, where L is a constant. We have already seen from Figure 3 that β decreases linearly with t_w , i.e., $\beta(t_w) = \beta_0(t_k - t_w)$. Substituting the t_w -dependence of β and the Arrhenius dependence of $L_0(t_w)$ in the expression for τ yields a VFT equation,

$$\begin{aligned} \tau &= t_0 \left[\frac{L \exp(t_w/t_\beta^\infty)}{t_0} \right]^{1/\beta} = L^{1/\beta} t_0^{(\beta-1)/\beta} \exp(t_w/\beta t_\beta^\infty) \\ &= C \exp\left(\frac{t_w}{t_\beta^\infty \beta_0(t_k - t_w)}\right), \end{aligned} \quad (5)$$

where $C = L^{1/\beta} t_0^{(\beta-1)/\beta}$. Equation (5) has an identical form as Equation (2), when $t_k \approx t_\alpha^\infty$, with τ diverging at $t_w \rightarrow t_\alpha^\infty$ and the width w of the distribution $\rho_{ww}(\tau)$ diverging simultaneously at t_k . This explains the correlation between t_k and t_α^∞ observed in Figure 4.

This successful adaptation of the coupling model, which was previously proposed for molecular glass formers, to the present scenario of aging colloidal Laponite suspensions,

clearly demonstrates the universal nature of the approach to a final arrested state in nonergodic systems. Additionally, the comparable behavior of fragility parameter D in these two systems and the use of the coupling model to explain the observed correlation between the two hypothetical divergence times t_α^∞ and t_k indicate a remarkable similarity of their relaxation processes at the particle scale.

IV. CONCLUSIONS

In this work, the time evolutions of the relaxation processes of colloidal suspensions of Laponite are studied by dynamic light scattering (DLS). The fragility parameter D is obtained by fitting the autocorrelation data $C(t)$ for Laponite suspensions of different concentrations (C_L), added salt concentrations (C_S) and temperatures (T). It is seen that the value of D is approximately constant for the entire range of Laponite concentrations and salt concentrations investigated here. These results are reminiscent of the observed independence of the isochoric fragilities of supercooled liquids on pressure.²⁸ Furthermore, D is seen to be independent of the screening effects of the repulsive interparticle interactions. Finally, it is established that T determines the rate at which system approaches the nonergodic transition (or the apparent cooling rate) and that D is weakly dependent on T . This result is reminiscent of the dependence of the kinetic fragility on the cooling rate for metallic glass formers.³³

The stretching exponents β for Laponite suspensions with different C_L , C_S , and T are seen to decrease linearly with waiting time, indicating a divergence of the width of the relaxation time distribution for very high waiting times. This observation is similar to the decrease of β with $1/T$ in many fragile molecular glass formers.¹⁶ We next define a time scale t_k at which the width of the distribution of the slow relaxation time scale diverges. We report a correlation between t_k and t_α^∞ , where t_α^∞ is the hypothetical Vogel time at which the average slow relaxation time diverges. This correlation corroborates analogous observations in fragile molecular glass formers for which it was reported that the Kauzmann and Vogel temperatures are approximately equal ($T_K \approx T_0$). We next calculate the ratio t_α^∞/t_k and plot it vs. D . This ratio is found to be approximately 1 for all the D values reported here. This observation is reminiscent of the change in the ratio T_K/T_0 with fragility parameter D seen for several supercooled liquids.³⁶

Our results therefore agree very well with existing results for fragile glass formers. Interestingly, in the case of Laponite suspensions, a colloidal system, t_k is measured from the kinetics of the relaxation process and signifies the time at which the width of the distribution of structural relaxation times diverges. In contrast, T_K for supercooled liquids is a thermodynamic quantity and generally calculated from calorimetric data. The correlation between the two hypothetical diverging time scales for Laponite suspensions, $t_k \approx t_\alpha^\infty$, demonstrates that the average value and the width of the distribution of slow relaxation times diverge simultaneously. We explain this result using the coupling model proposed for molecular glass formers⁴⁰ and the t_w -dependence of the stretching exponent β observed in our experiments.

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