

Thermally activated asymmetric structural recovery in a soft glassy nano-clay suspension†

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In this work we study the structural recovery of a soft glassy Laponite suspension by monitoring temporal evolution of elastic modulus under isothermal conditions as well as following step temperature jumps. Interestingly, evolution behavior under isothermal conditions indicates the rate, and not the path of structural recovery, to be dependent on temperature. The experiments carried out under temperature jump conditions however trace a different path of structural recovery, which shows strong dependence on temperature and the direction of change. Further investigation of the system suggests that this behavior can be attributed to the restricted mobility of counterions associated with Laponite particles at the time of temperature change, which do not allow the counterion concentration to reach the equilibrium value associated with the changed temperature. Interestingly this effect is observed to be comparable with other glassy molecular and soft materials, which while they evolve in a self-similar fashion under isothermal conditions show asymmetric behavior upon temperature change.

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1 Introduction

Glassy materials, such as molecular and soft (colloidal) glasses, are out of thermodynamic equilibrium owing to the constrained mobility of the trapped constituting entities. In molecular glasses a kinetically arrested state is achieved by rapidly decreasing the temperature, while in soft glasses the same is obtained by rapidly increasing the concentration of constituents or by altering the inter-particle interactions.¹ Under quiescent conditions, these materials undergo structural organization as a function of time. This process is known as physical aging or structural recovery.^{2–4} During this process, the molecular glasses typically undergo specific volume relaxation (or densification) as a function of time. Aging or structural recovery in soft glasses, on the other hand, can be represented merely as progressive reduction in free energy as a function of time, as there is no generic structural variable associated with this process.⁵ In any glassy material, temperature is an important variable that affects the timescale of structural organization, and its effect on molecular glasses has been studied in great detail.⁶ In this work we study how physical aging in a soft glassy nano-clay (Laponite RD) suspension is affected by change in temperature, and the similarity it shares with structural recovery in molecular and other colloidal glasses.

In order to have physical aging in the materials arrested in a thermodynamically out of equilibrium state, the trapped entities must possess sufficient kinetic (thermal) energy to carry out structural organization. The extreme case of total absence of thermal energy in the trapped entities is randomly packed stationary granular media, wherein the aging is completely absent, and the system remains arrested in the high energy state forever. Enhancement in thermal energy caused by an increase in temperature is observed to expedite the aging process in the molecular glasses^{6–8} as well as in the soft glassy materials.^{9–12} However, depending upon the precise nature of structural rearrangement present during the physical aging and the nature of low energy structures, additional effects triggered by the change in temperature may also influence this process. One of the standard ways to assess the influence of other temperature dependent variables on structural recovery is to induce step-up and step-down temperature jumps and follow the evolution of the affected variable as a function of time. For example, classical experiments by Kovacs⁷ demonstrated that specific volume relaxation of polymeric glasses upon step-up and step-down change in temperature follows asymmetric paths. This behavior is explained by competition between filled volume dilation/shrinkage and free volume equilibration upon temperature change. The asymmetry arises because filled volume dilation is restricted by the free volume change in the step-up jump, but filled volume shrinkage is not restricted by free volume change in the step-down jump.¹³ Recently McKenna and co-workers¹⁰ carried out similar experiments but on a soft colloidal glass composed of thermoresponsive particles of poly(*N*-isopropylacrylamide). These particles show rapid

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swelling/shrinkage dynamics and the volume of the same can be tuned by changing the temperature (diameter of particles decreases by increasing temperature). Interestingly this system also showed the qualitative features of asymmetry upon step-up and step-down jumps in the volume fraction of particles triggered by change in temperature.

In this work we study how the structural recovery behavior of an aqueous suspension of Laponite RD, a model soft glassy material, is affected by step-up and step-down temperature jumps. The primary particle of synthetic clay Laponite RD has a disk-like shape with a diameter of 25 ± 2.5 nm and a thickness of 1 nm.¹⁴ This material is also known to have very low size polydispersity.¹⁵ A disk of Laponite constitutes three layers wherein two tetrahedral silica layers sandwich an octahedral magnesia layer. Isomorphous substitution of magnesium by lithium induces scarcity of positive charge such that the face of a Laponite particle acquires a permanent negative charge.¹⁶ In powder form Laponite particles are present in stacks with sodium ion residing in the interlayer gallery. After dispersing in water, clay layers swell and owing to osmotic pressure gradient, sodium ions dissociate in water thereby exposing negatively charged faces.¹⁷ At pH 10, the edge of a Laponite particle has a weak positive charge.¹⁸ Overall three types of interactions are present among the Laponite particles in the aqueous media namely,⁵ repulsion among the faces, attraction between the edge and the face, and van der Waals attraction among the particles. These interactions are responsible for the soft glassy nature of the Laponite suspension and influence its phase behavior and structural recovery.

II Experimental procedure

We procured Laponite RD® from Southern Clay Products Inc. White powder of Laponite was dried at 120 °C for 4 hours before mixing with ultrapure water having pH 10. A detailed procedure to prepare a Laponite suspension has been described elsewhere.⁵ Freshly prepared unfiltered 2.8 weight% Laponite suspension was preserved in an air sealed polypropylene bottle for 3 months before using the same. The rheological experiments were performed using the MCR 501 rheometer (Couette geometry: outer diameter 5.4 mm with a gap of 0.2 mm). In a typical experiment the sample was shear melted using oscillatory strain ($\gamma_0 = 7000$ and frequency 0.1 Hz for 20 min). Subsequently oscillatory shear stress ($\sigma = 1$ Pa, frequency 0.1 Hz) was applied to monitor the evolution of viscoelastic behavior in the isothermal as well as in the temperature step change experiments. We verified that application of an oscillatory flow field with a stress magnitude of 1 Pa does not affect the aging process. We also measured the ionic conductivity of Laponite suspension samples using a Eutech Cyberscan CON 6000 conductivity meter with a 4 cell electrode (range 0–500 mS and temperature range 0–70 °C). We measured the conductivity at constant temperatures from 1 to 40 °C as well as in temperature step change experiments. We carried out the conductivity experiments in the rheometer cell itself so as to identically match the temperature change profiles in the rheology experiments.

III Results and discussion

In Fig. 1 we plot the evolution of elastic modulus as a function of time elapsed since stopping the shear melting (aging time) at five temperatures for the Laponite suspension. It can be seen that the evolution of elastic modulus shifts to lower aging times for experiments carried out at higher temperatures. The self-similar curvature of G' allows the formation of superposition mainly by horizontal shifting. In a glassy material, constituents of the same are kinetically arrested in physical cages formed by neighbors, which allow only a restricted access to its phase space causing ergodicity breaking. In the process of physical aging the material explores its phase space and progressively attains lower values of free energy as a function of time. If we represent individual physical cages as energy wells, lowering of free energy as a function of time is equivalent to the increase in well depth. If E is the average energy well depth, then through scaling arguments elastic modulus of a material can be written as: $G' \propto E/b^3$, where b is the characteristic length.¹⁹ Furthermore, the timescale associated with the process of aging, also known as microscopic timescale (τ_m), determines the rate at which the average energy well depth E increases: $E = E(t/\tau_m)$. Owing to faster thermal motions, τ_m is expected to decrease with an increase in temperature. An increase in G' can be therefore considered as an indication of a decrease in free energy,⁵ and the time dependence of the same can be given by:

$$G'(T, t) = G(T)g(t/\tau_m). \quad (1)$$

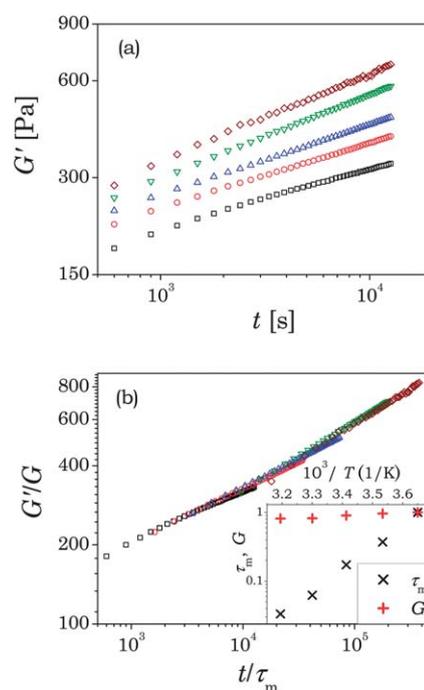


Fig. 1 (a) Evolution of G' as a function of time for different temperatures (diamonds 40 °C, down triangles 30 °C, up triangles 20 °C, circles 10 °C and squares 1 °C). (b) Superposition of the evolution obtained at different temperatures. The inset shows the variation of shift factors as a function of inverse of temperature required to obtain the superposition.

If we introduce $\tilde{G}' = G'/G(T)$ and $x = t/\tau_m$, eqn (1) can be simply written as:

$$\tilde{G}' = g(x). \quad (1a)$$

The superposition shown in Fig. 1(b) essentially represents the function form of eqn (1a) with G and τ_m as vertical and horizontal shift factors respectively. We arbitrarily set $G(T_R) = 1$ Pa and $\tau_m(T_R) = 1$ s, where T_R is the reference temperature ($T_R = 1^\circ\text{C}$) as shown in the inset of Fig. 1(b). τ_m is observed to increase with $1/T$ (τ_m can be seen to be following Arrhenius dependence, however the experimentally explored range of $1/T$ is very limited). The vertical shifting is necessary as an increase in temperature is observed to decrease modulus in addition to its effect on τ_m . The vertical shift factor $G(T)$ was always closer to unity as shown in the inset.

In Fig. 2, we plot the effect of step-up and step-down temperature jump on the evolution of G' as a function of time. In both the cases the temperature was changed at 1800 s. We have omitted the G' data associated with the transient in temperature. (For complete raw data refer to the ESI†) Fig. 2(a) shows that greater the decrease in temperature is, lower is the rate of evolution of G' . Alternatively, Fig. 2(b) shows that larger the increase in temperature is, faster is the evolution of G' . This scenario is described more clearly in Fig. 3, where the evolution of G' at 1, 20 and 40 °C is shown in addition to that associated with 1 to 20 °C and 40 to 20 °C step changes. It can be seen that both the step change data approach the 20 °C evolution curve. In Fig. 2 and 3, immediately after the step increase in temperature, G' can be seen to be decreasing below the isothermal aging curve of the previous temperature. This is due to inverse dependence of G' on temperature. However, since the aging rate is greater at a high temperature it soon crosses the isothermal aging curve of the previous temperature. Equivalently G' is expected to increase immediately after a decrease in temperature; however this behavior has been masked by transient in temperature, for which we have not reported the data (refer to the ESI† for more details).

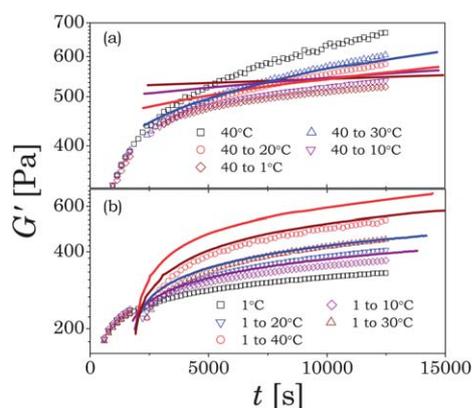


Fig. 2 Evolution of G' upon step jump in temperature at 1800 s. The top figure (a) describes the behavior for step-down jump from 40 °C to the mentioned lower temperatures, while the bottom figure (b) describes step-up jump from 1 °C to the mentioned higher temperatures. Lines passing through the data represent the predictions of eqn (2) and (3) that use the isothermal aging data.

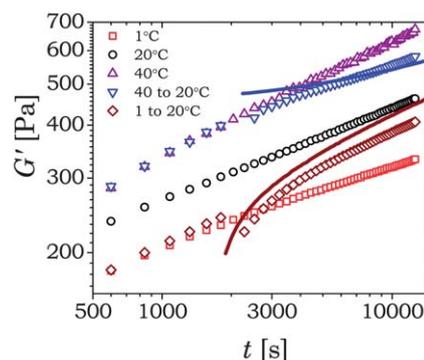


Fig. 3 Evolution of G' at 1, 20 and 40 °C and after a step-down jump (40 to 20 °C) and a step-up jump (1 to 20 °C) at 1800 s. The lines passing through the data represent predictions using isothermal evolutions and eqn (2) and (3).

An assumption that G' follows eqn (1) suggests that a change in temperature does not change the path of aging, but only the rate at which aging takes place. If such a scenario exists, the knowledge of evolution of G' at one temperature, along with the dependences of τ_m and G on T , can be used to predict not just evolution at any other temperature but also the evolution associated with a step change. Let us assume that a step change in temperature from T_1 to T_2 was introduced at time t_1 . However, on \tilde{G}' versus x ($G'/G(T)$ versus t/τ_m) scale, the material will continue to age on the same path, except with a different rate beyond time t_1 . Therefore the state of the material undergoing aging at temperature T_1 for time t_1 is the same as at time t_2 if aging would have been carried out at temperature T_2 since the beginning ($x = t_1/\tau_{m1} = t_2/\tau_{m2}$, where τ_{mi} is associated with temperature T_i). Therefore, t_2 is given by:

$$t_2 = (\tau_{m2}/\tau_{m1})t_1. \quad (2)$$

The value of \tilde{G}' at time t after the temperature step jump ($t > t_1$) can then simply be represented by:

$$\tilde{G}' = g(x_1 + x_2), \quad (3)$$

where $x_1 = t_1/\tau_{m1}$ and $x_2 = (t - t_1)/\tau_{m2}$. Evolution of G' after the step jump can then be written in terms of τ_m associated with the changed temperature using eqn (2) and (3) to yield:

$$G' = G'(T_2, t - (t_1 - t_2)) = G(T_2)g([(t - (t_1 - t_2))/\tau_{m2}] \text{ for } t \geq t_1. \quad (3a)$$

The above analysis suggests that the knowledge of evolution of G' under isothermal conditions and shift factors at different temperatures should facilitate the prediction of evolution after the step change through eqn (3). We therefore use data presented in Fig. 1 to predict the evolution of G' after the step change in temperature in Fig. 2 and 3. The prediction has been described using thick lines. We have used $t_1 = 1920$ s for the step-up data and 2200 s for the step-down data, which is different from the actual value of $t_1 = 1800$ s owing to finite time required to complete the step change. It can be seen that eqn (2) and (3) significantly over predict the evolution of G' subsequent to the step-up temperature change. On the other hand predictions of

step-down temperature change associated with 40 °C to 20 °C, 10 °C and 1 °C cross each other and do not follow the curvatures of the respective experimental data. Interestingly the prediction of 40 °C to 30 °C comes closest to the experimental data.

The above discussion suggests that the assumption of eqn (1) results in an excellent superposition (Fig. 1); but its logical extension, which leads to eqn (3), fails to predict the evolution subsequent to the temperature change. Consequently, this result indicates that on $G'/G(T)$ versus t/τ_m scale the material will not continue to age on the same path upon the change in temperature. This further suggests the possibility of physicochemical changes to the Laponite suspension upon temperature change which may be irreversible over the experimental timescales.

Very recently it has been reported that the ionic conductivity of the Laponite suspension increases with an increase in temperature.⁵ The ionic conductivity of an aqueous Laponite suspension originates from NaOH used to maintain pH 10 of water and the sodium counterions (Na^+) associated with Laponite particles. The ionic conductivity of ultrapure water having pH 10 (maintained by adding NaOH) is around $20 \mu\text{S cm}^{-1}$. Therefore an increase in conductivity beyond this is due to dissociation of the Na^+ counterions from Laponite particles. In order to study the counterion (Na^+) dissociation behavior of the Laponite suspension upon temperature change, we measured the ionic conductivity of the same under isothermal conditions as well as upon temperature step change. The behavior of conductivity variation is shown in Fig. 4. Typically the measured values of conductivity of the suspension are over 40 times higher than the value associated with water having pH 10. Therefore a major contribution to ionic conductivity is from counterions. It should be noted that before measuring the ionic conductivity, suspension samples were

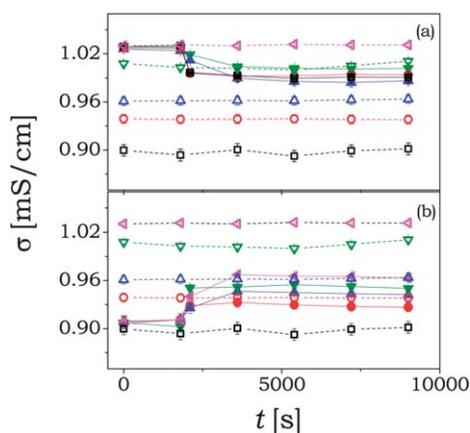


Fig. 4 Ionic conductivity of the Laponite suspension is plotted as a function of time under isothermal conditions (open symbols) and following the temperature change conditions (filled symbols). The temperature change was carried out at 1800 s. In both figures the open symbols from bottom to top: 1 °C, 10 °C, 20 °C, 30 °C, and 40 °C. Filled symbols in (a) represent the temperature down jump: black squares 40–1 °C, red circles 40–10 °C, blue up triangles 40–20 °C, and green down triangles 40–30 °C. The filled symbols in (b) represent the temperature up jump: red circles 1–10 °C, blue up triangles 1–20 °C, green down triangles 1–30 °C, and magenta left triangles 1–40 °C.

mechanically rejuvenated at the respective temperatures. The conductivity reported in Fig. 4 is under quiescent conditions and measured as a function of time after the mechanical rejuvenation was stopped. It can be seen from Fig. 4 that the conductivity of suspension kept under isothermal conditions remains constant over the duration of the experiment, but indeed increases with an increase in temperature. We also plot conductivity upon step change in temperature in the same plots without disturbing the material as is the case with rheology experiments. It can be seen that upon temperature step-up and step-down change, conductivity respectively increases and decreases subsequent to the change, but does not reach the same value associated with the isothermal measurements of the changed temperature. In addition, for smaller changes in temperature the difference of the isothermal conductivity value and that upon temperature change is small, but increases with an increase in the magnitude of temperature change.

Usually subsequent to the temperature change, the ionic conductivity (or the concentration of counterions) is expected to equilibrate with respect to the changed temperature. In the case of an increase in temperature more dissociation of counterions and their diffusion away from the particle surface is expected. On the other hand with a decrease in temperature part of the counterions are expected to recombine with the faces of the Laponite particle. Therefore, the plausible reason behind the difference in counterion concentration under isothermal conditions and that after temperature change may be the soft solid like consistency associated with the Laponite suspension at the time of temperature change. In the conductivity experiments we ensure thermal equilibrium before the mechanical rejuvenation is performed. During the mechanical rejuvenation the material is in a liquid state and has low viscosity, consequently the mobility of the counterions is high and the equilibrium value of ionic conductivity associated with the corresponding temperature is achieved. However, at the time of temperature change the material is not in the liquid state but in an apparent solid state (G' is much above 200 Pa and significantly greater than G'') and owing to which reduction in the mobility of the counterions may take place. Such reduction in the mobility of counterions leads to restricted diffusion of counterions hindering achievement of equilibration of conductivity in the temperature step change experiments. Consequently, in temperature step-down experiments conductivity remains at a high value even at reduced temperature, while in step-up experiments conductivity remains at a low value though the temperature is high. We believe that this phenomenon is responsible for asymmetry in the rheological behavior in the up and down temperature jump experiments.

The concentration of counterions is known to profoundly influence interactions among the Laponite particles as it directly affects the Debye screening length ($1/\kappa$) as well as the surface potential (Φ_0) associated with the faces of Laponite particles. Typically the dependence of Debye screening length on the concentration of Na^+ ions is given by: $1/\kappa \sim n_{\text{Na}}^{-0.5}$,²⁰ while that of the surface potential is given by: $\Phi_0 \sim (n_{\text{Na}} - n_0)$,⁵ where n_0 is the number density of Na^+ ions due to the sources other than Laponite (such as NaOH). Shahin and Joshi⁵ recently

analyzed interactions among the Laponite particles using DLVO theory and observed that enhancement in conductivity owing to counterions increases the height of the repulsive energy barrier, however it decreases the width of the same when particles approach each other in a face-to-face fashion. Therefore, due to the difference in conductivity associated with isothermal and temperature change experiments, eqn (2) and in turn eqn (3) cannot be applied to the same.

From the comparison of the predictions of eqn (3) and the experimental data shown in Fig. 2, it is plausible to conclude that a decrease in concentration of Na^+ ions causes an increase in G' . This is more apparent for the comparison of step-down temperature change experiments (for step-up temperature change experiments this effect is observable over a small duration of time). In Fig. 2, prediction subsequent to a step-down temperature jump shows a higher increase in G' for a greater decrease in T as the model considers isothermal data for which the concentration of Na^+ ions substantially decreases with a decrease in T . As time passes, owing to a higher rate of aging at higher T , the predictions cross each other. A qualitatively similar behavior is also observed for step-up temperature jump predictions with cross over occurring soon after the temperature change. In reality, however, a decrease in temperature does not decrease the concentration of Na^+ ions to the level of isothermal values. Consequently, the increase in G' in step-down experiments and the decrease in G' in step-up experiments are significantly smaller than those predicted by the model. Interestingly the conductivity after the temperature step-down jump from 40 °C to 30 °C is very similar to that of the isothermal conductivity associated with 30 °C as shown in Fig. 4(a). As a result, we can apply eqn (2) and (3) to the G' evolution data. Consequently, as shown in Fig. 2, the prediction of the behavior upon temperature change for 40 °C to 30 °C comes closest to that of experimental data.

In soft glassy materials the interparticle interactions are primarily responsible for their inability to achieve equilibrium.¹ Therefore for those soft glassy materials, where the constituents of the same bear dissociable counterions and charged surfaces, the hindered mobility of the ions cannot be ruled out. For such systems aging behavior upon step temperature change can be similar to that observed in the present work. The present results therefore suggest an apparent similarity with the observation of asymmetric structural recovery seen in the polymeric glasses as reported by Kovacs⁷ and for thermo-sensitive soft glassy paste as observed by McKenna and co-workers.¹⁰ In all these cases asymmetry can be attributed to other nonlinear physical effects induced due to the change in temperature. However these other nonlinear effects originate from the kinetically arrested nature of the material. In the first case it is asymmetric dissociation of counterions upon change in temperature while in the latter cases it is asymmetry associated with filled volume expansion/contraction triggered by the temperature change.

IV Conclusion

In this work, we monitor the evolution of G' of a shear rejuvenated soft glassy Laponite suspension under isothermal as well

as step temperature change experiments. It is typically observed that structural recovery described by an increase in G' is faster at greater temperatures, and speeds up or slows down respectively for the step-up and step-down changes in temperature. The superposition of isothermal evolution curves of G' at different temperatures supports an assumption that only the rate of structural recovery and not the path depends on temperature. However, when temperature change is carried out in the solid state, this assumption fails to predict the evolution of G' following step change from the isothermal data, suggesting that temperature change induces such effects that are irreversible over the observation timescales. We also measure the ionic conductivity of the Laponite suspension which indicates the concentration of dissociated counterions. For experiments carried out at constant temperatures, conductivity is observed to be higher at greater temperatures. However during the temperature jump experiments, owing to the restricted mobility of the ions at the time of jump when the material is in a solid state, the change in conductivity does not reach the isothermal conductivity values associated with the changed temperature. We feel that this nonlinearity associated with conductivity change causes rheological response to be asymmetric.

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