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Rheological behaviour of aqueous suspensions of laponite: new insights into the ageing phenomena

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In this paper, the ageing behaviour of suspensions of laponite with varying salt concentration is investigated using rheological tools. It is observed that ageing is accompanied by an increase in the complex viscosity. The creep experiments performed at various ages show damped oscillations in the strain. The characteristic time scale of the damped oscillations, the retardation time, shows a prominent decrease with increasing age of the system. However, this dependence weakens with an increase in the salt concentration, which is known to change the microstructure of the system from glass like to gel like. We postulate that a decrease in the retardation time can be represented as a decrease in the viscosity (friction) of the dissipative environment surrounding the arrested entities that oppose elastic deformation of the system. We believe that ageing in colloidal glass leads to a greater ordering that enhances relative spacing between the constituents, thereby reducing the frictional resistance. However, since a gel state is inherently different in structure (fractal network) to that of a glass state (disordered), ageing in the gel does not induce ordering. Consequently, we observe an inverse dependence of retardation time on age, which becomes weaker with an increase in the salt concentration. We analyse these results from the perspective of ageing dynamics of both glass and gel states of laponite suspensions.

Keywords: clay suspensions; ageing; colloidal glasses and gels; thixotropy

1. Introduction

Glassy state is generally referred to a state, wherein the system explores only a part of the phase space available to it (Liu & Nagel 1998). Despite many decades of active research aimed at improving our understanding of these systems, various intriguing features of the glassy state dynamics are still poorly understood, and thus continue to attract significant attention from the physics, biology and engineering community (Cipelletti & Ramos 2005; Sciortino & Tartaglia 2005). Apart from molecular glass formers, non-ergodic systems that dominate the present research activity in this field include colloidal suspensions

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Dedicated to Dr R. A. Mashelkar, on the occasion of his 65th birthday.

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(Weeks *et al.* 2007), polymer–clay composites (Treece & Oberhauser 2007), emulsions (Gang *et al.* 1999), gels (Cloitre *et al.* 2003), foams (Cohen-Addad & Hohler 2001), block copolymers (Mallamace *et al.* 2000), etc. In addition to the significant academic interest in understanding the glassy state dynamics in these systems, their industrial applications have provided further impetus for such studies.

In this work, we investigate the ageing dynamics of aqueous laponite suspensions using rheological tools. Laponite is composed of disc-shaped nanoparticles with a diameter 25 nm and layer thickness 1 nm (Kroon *et al.* 1998). The chemical formula for laponite is $\mathrm{Na^{+}}_{0.7}[(\mathrm{Si_8Mg_{5.5}Li_{0.3}})\mathrm{O_{20}(OH)_4}]^{-}{}_{0.7}$. An isomorphic substitution of magnesium by lithium atoms generates negative charge on its surface, which is counterbalanced by the positive charge of the sodium ions present in the interlayer (Van Olphen 1977). In an aqueous medium, sodium ions dissociate which, in turn, leads to a net negative charge on its surface. The edge of the laponite particle is composed of hydrous oxide, and its charge is less negative in the basic medium, while it is positive in the acidic medium (Van Olphen 1977). Its suspension in the aqueous medium leads to the formation of non-ergodic soft solids that show a rich variety of physical behaviour.

Aqueous laponite suspensions display a very rich phase behaviour, and different groups have proposed various versions of phase diagrams for laponite with respect to the concentrations of the salt and the laponite (Mourchid *et al.* 1995*a*; Gabriel *et al.* 1996; Tanaka *et al.* 2004; Mongondry *et al.* 2005; Michott *et al.* 2006; Ruzicka *et al.* 2006, 2007). In the salt-free aqueous medium and at pH 10 (approx. 10^{-4} M $\mathrm{Na^+}$ ions), the electrostatic screening length associated with a laponite particle is approximately 30 nm (Bonn *et al.* 1999). Under such conditions, the net interaction between various laponite particles is repulsive in nature. It is generally believed that, for concentrations above 1 wt% and in the near absence of any salt in the system (or below 10^{-4} M concentration of $\mathrm{Na^+}$ ions), ergodicity breaking leads to the formation of the repulsive (Wigner) glasses (Bonn *et al.* 1998; Knaebel *et al.* 2000; Levitz *et al.* 2000; Tanaka *et al.* 2004). On the other hand, the addition of a salt to a laponite suspension increases the concentration of cations in the system, which screen the negative charges on the laponite particle, thereby changing the state of the system from being a repulsive glass to a gel (Avery & Ramsay 1986; Mourchid *et al.* 1995*a*,*b*; Kroon *et al.* 1996, 1998; Pignon *et al.* 1996, 1997*a*,*b*; Nicolai & Cocard 2000, 2001; Mongondry *et al.* 2005). At higher concentrations of laponite, the system enters into a nematic phase (Gabriel *et al.* 1996; Bhatia *et al.* 2003; Ravi Kumar *et al.* submitted). Generally, a glassy state is distinguished from a gel state based on the presence of a fractal network in the latter, while in the case of the former, density is uniform for probed length scales greater than the particle length scale (including the Debye screening length).

During the past few years, several groups have studied the ergodic–non-ergodic transition of a laponite suspension at low ionic concentrations using various optical and rheological techniques (Mongondry *et al.* 2005; Tanaka *et al.* 2005; Ruzicka *et al.* 2006; Schosseler *et al.* 2006). A common procedure is to pass the laponite dispersions through microfilters to study the structural evolution with respect to its ‘age’. It is generally acknowledged that the filtration influences their optical characteristics but not their rheological response (Bonn *et al.* 1999). It is observed that the system has two relaxation modes. The fast or β mode is observed to be independent of the age of the sample (Abou *et al.* 2001; Bellour *et al.* 2003); however, Ruzicka *et al.* (2004) have recently reported a slight increase in this mode with age in the low-concentration regime (less than 1.5–1.8 wt%). The slow or α mode of relaxation shows an initial rapid increase followed by a linear increase with age (Abou *et al.* 2001; Bellour *et al.* 2003; Tanaka *et al.* 2005; Schosseler *et al.* 2006). The sub-regime with a rapid initial increase is called a cage-forming regime, while the latter regime is called the full ageing regime (Tanaka *et al.* 2005). Recently, Joshi (2007) proposed that the rapid increase in the relaxation time with age in the cage formation regime is due to the osmotic swelling of laponite clusters that are formed immediately after the preparation of the sample.

Owing to the widespread applications of aqueous clay suspensions, significant work has been carried out on their rheological characterization. Most of the early studies concentrated on thixotropy, yield stress and pumpability of these materials. Van Olphen (1977) and, more recently, Barnes (1997) and Luckham & Rossi (1999) have all presented excellent state-of-the-art accounts of most of the previous rheological works available in the literature. Very recently, Coussot (2006, 2007) has provided an excellent summary of recent literature on rheological behaviour and modelling approaches of ageing dynamics of soft non-ergodic materials including clay suspensions. Lately, the focus of various studies is dominated by understanding the microstructural description through rheological measurements. Cocard *et al.* (2000) studied the frequency dependence of the time evolution of the elastic modulus for an ageing laponite suspension that is in a gel state at various salt concentrations. They also observed that frequency dependence of the elastic and viscous moduli, which is similar to that of a viscous liquid at a small age, weakens with age (or gelation time). They observed that the rate of gelation increases with ionic strength. Bonn *et al.* (2002*b*) studied aqueous laponite suspensions in a basic medium using *in situ* diffusive wave spectroscopy. They observed that the viscosity dependence of age directly correlates with the slow mode relaxation time dependence of age. Subsequently, in a similar observation to that of Cocard *et al.* (2000), Bonn *et al.* (2002*a*) reported that immediately after sample preparation, the frequency dependence of the viscous and elastic moduli is similar to that of a viscous liquid. Eventually, both moduli become independent of the frequency as the glass transition is approached. Mourchid *et al.* (1995*a*) used the shear rheology to monitor sol–gel transition in laponite suspensions, and observed that increasing the ionic strength shifts the sol–gel transition to a lower volume fraction.

In creep experiments, many soft glassy systems show damped oscillations in strain due to coupling between the viscoelastic behaviour of the fluid and the inertia of the instrument. Baravian & Quemada (1998) systematically analysed such inertial oscillations using various linear viscoelastic mechanical models. Subsequently, Baravian *et al.* (2003) studied the creep behaviour of aqueous montmorillonite suspensions. By analysing the inertial oscillations, they estimated the high-frequency elastic modulus of the system, which otherwise was not possible using conventional oscillatory tests. Recently, Coussot *et al.* (2006) studied three complex fluids, namely an aqueous bentonite suspension, mustard and hair gel, using creep experiments and observed oscillations in strain, which attenuate rapidly. They estimated that the elastic modulus of the system shows a logarithmic dependence on age. In subsequent work, Ovarlez & Coussot (2007) studied the effect of temperature, density and concentration on the ageing behaviour of aqueous bentonite suspension. They observed that all the elastic modulus versus time curves fall on a single master curve when rescaled by a factor that is a function of concentration, temperature, strength of deformation and age of the system, thus demonstrating equivalence of these parameters in the context of ageing behaviour. Recently, Joshi & Reddy (submitted) carried out systematic creep experiments on ageing soft solids of laponite at various ages and stresses. They observed that when imposed time is normalized by the dominant relaxation mode of the system, which depends on age and stress, a universal master curve for creep that is invariant of applied stress and age of the system is obtained. Similarly, in recent years considerable work has been carried out to understand the rejuvenation phenomena *per se* in soft glassy systems (Cloitre *et al.* 2000; Bonn *et al.* 2002*b*; Viasnoff & Lequeux 2002; Abou *et al.* 2003; Di Leonardo *et al.* 2005; Ianni *et al.* 2007). However, various features of such ageing systems as over-ageing (Viasnoff & Lequeux 2002), multiple decoupled time scales and their distribution (Abou *et al.* 2001), complicated energy landscapes leading to multiple ageing paths (Jabbari-Farouji *et al.* 2007), fast ageing dynamics of rejuvenated systems (Ianni *et al.* 2007) and inapplicability of time translational invariance (Fielding *et al.* 2000) demand further study and understanding of the ageing phenomena.

In this work, we perform oscillatory and creep experiments on laponite suspensions to investigate their ageing dynamics after carrying out a specific rejuvenation procedure. In particular, we exploit the information embedded in the damped oscillations of strain in creep to estimate the retardation time of the system. Retardation time represents resistance offered by the microstructure to the elastic deformation of the system. As the retardation time tends to zero, meaning no resistance, the system response becomes perfectly elastic. We observe that as the system ages, although the resistance to translational diffusion significantly increases, at a local level, the friction decreases leading to a lowering of the retardation time with age. Furthermore, we also analyse the dependence of the retardation time on the age of the system and molar concentration of the salt, which reveal distinguishable characteristics of ageing in glasses and gels. We believe that this information provides further useful insights into the underlying microscopic phenomena in the process of ageing in such systems.

2. Preparation and viscometry

Laponite RD, synthetic hectorite clay, used in this study was procured from Southern Clay Products, Inc. A predetermined specific molar concentration of Na^+ ions was maintained by adding NaCl to ultrapure water. The white powder of laponite was dried for 4 h at 120°C before mixing it with water at pH 10 under vigorous stirring conditions. The basic pH (approx. 10) was maintained by the addition of NaOH to provide chemical stability to the suspension. The suspension was stirred vigorously for 15 min. We have used seven systems; six systems have 3.5 wt% laponite and 10^{-4}, 10^{-3}, 3×10^{-3}, 5×10^{-3}, 7×10^{-3} and 10^{-2} M concentration of Na^+ ions, while the seventh system has 2 wt% laponite and 10^{-2} M concentration of the Na^+ ions.

In this work, stress-controlled oscillatory shear and creep experiments were carried out using a stress-controlled rheometer, AR 1000 (couette geometry, bob diameter 28 mm with a gap of 1 mm). The couette cell was filled up with the test sample and 3.5% 10^{-4} and 2.0% 10^{-2} M samples were left to age for 3 h, while 3.5% 10^{-3}, 3×10^{-3}, 5×10^{-3}, 7×10^{-3} and 10^{-2} M samples were left to age for 90 min. To avoid the loss of water by evaporation or the possibility of CO_2 contamination of the sample, the free surface of the suspension was covered with a thin layer of a low-viscosity silicon oil during the course of viscometric measurements. Subsequently, we applied an oscillatory deformation with stress amplitude of 50 Pa and frequency 0.1 Hz for approximately 600–1100 s, unless otherwise mentioned. As expected, the suspension yields under such a high stress and eventually shows a plateau of low viscosity that does not change with time. We stopped the rejuvenation (shear melting) experiment at this point in time, from which the ageing time was measured. Subsequent to rejuvenation, we carried out the stress-controlled oscillatory shear experiments by employing a shear stress amplitude of 0.5 Pa and frequency 0.1 Hz to record the ageing behaviour of this system. In all creep experiments, we have applied a constant stress of 1.5 Pa for 100 s, unless otherwise mentioned. All results reported in this paper relate to 20°C. We also carried out additional frequency sweep experiments on independent samples at the end of the waiting period. It was observed that the storage modulus was independent of the frequency, while the loss modulus showed a slight decrease with frequency in the experimentally accessible frequency range. This observation is in line with the findings of Bonn *et al.* (2002*a*), and, according to Fielding *et al.* (2000), this ensures the system to be in the non-ergodic regime.

3. Results and discussion

In this work, we have employed a specific experimental protocol to study the ageing behaviour of a laponite suspension. Freshly prepared laponite samples were left idle for a fixed period of time as mentioned in §2 in a couette geometry, prior to being subjected to a rejuvenation (shear melting) experiment by applying an oscillatory stress of 50 Pa. Figure 1 shows a typical shear rejuvenation behaviour for several independent (freshly prepared) samples of 3.5% 10^{-3} M laponite suspension. It can be seen that initially the viscosity gradually decreases; this is followed by a very sharp decrease until a plateau is reached, which does not change with time. For this system, we have varied the rejuvenation time from 600 to 900 s; however, each experiment was stopped only after the plateau was reached. The inset in figure 1 shows the corresponding ageing curves where the age is measured after the rejuvenation experiment is stopped. It can be seen that the ageing behaviour is relatively insensitive to the minor variations in the rejuvenation step. In the shear rejuvenation experiments, the primary harmonic in strain was at least an order of magnitude larger than the third harmonic, and hence it is justifiable to analyse these data in terms of a complex viscosity. Figure 2 shows a typical shear rejuvenation and the subsequent ageing behaviour for several independent samples of 3.5% 5×10^{-3} M laponite suspension. Since the stress of 50 Pa was not sufficient to cause yielding in this system, an oscillatory stress with a magnitude of 70 Pa was employed. Interestingly, this system shows yielding in two stages, with an intermediate plateau occurring at a complex viscosity of approximately 5 Pa s. For one sample (shown in filled

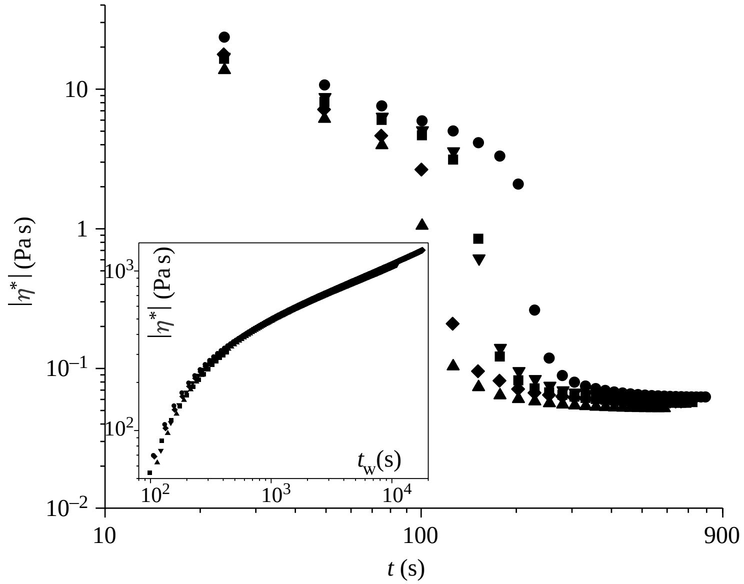

Figure 1. Rejuvenation data for 3.5% 10^{-3} M laponite suspension. Rejuvenation was carried out at a stress amplitude of 50 Pa. The inset shows corresponding ageing curves at a stress amplitude of 0.5 Pa, which is carried out subsequent to the rejuvenation experiment. Same symbols are used for rejuvenation and ageing of the same sample.

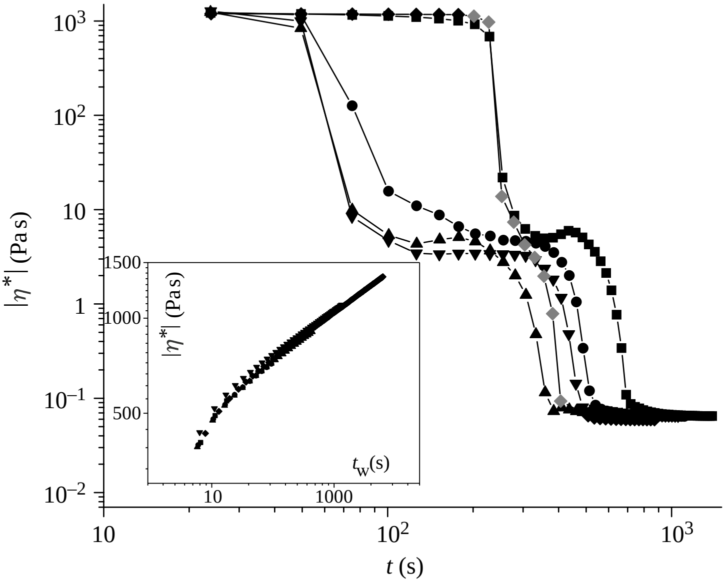

Figure 2. Rejuvenation data for 3.5% 5×10^{-3} M laponite suspension. Rejuvenation was carried out at a stress amplitude of 70 Pa. For filled diamonds, an initial stress amplitude of 70 Pa was used. It was changed to 80 Pa for a brief period of time and changed back to 70 Pa again (refer to text for details). The points for which 80 Pa stress amplitude was employed are shown in grey shade. The line is a guide to the eye. The inset shows corresponding ageing curves at a stress amplitude of 0.5 Pa that is carried out subsequent to rejuvenation experiment. Same symbols are used for rejuvenation and ageing of the same sample.

diamonds), an oscillatory stress of 70 Pa was applied for 178 s followed by 80 Pa for 307 s and 70 Pa for 386 s, in order to avoid the formation of an intermediate plateau. The data for which the 80 Pa stress was applied are shown in grey shade in the same figure. A subsequent ageing curve is shown in an inset where an oscillatory stress of 0.5 Pa was employed. It can be seen that the various ageing curves are very similar irrespective of the differences inherent in the rejuvenation step. For the 3.5% 7×10^{-3} and 10^{-2} M laponite suspensions, we used different stress amplitudes to rejuvenate the samples and, however, observed no difference in the ageing behaviour. For the 2% system at 10^{-2} M ionic concentration, we employed a stress amplitude of 40 Pa in the rejuvenation step.

An important feature of the rejuvenation step can be summarized as follows: once a plateau of low viscosity is reached (which does not change with time), the ageing behaviour of the system becomes independent of the minor differences and the time elapsed during the rejuvenation experiment. In the ageing system, various properties of the system are known to evolve with age. In general, it is observed that the characteristic (dominant) relaxation time of the system changes with age as $\tau_\alpha \sim t_{\mathrm{w}}^{\mu}$, where t_{w} is the age and μ is a positive constant (Struik 1978; Cloitre *et al.* 2000; Fielding *et al.* 2000). Struik (1978) suggested that in the limit $\mu \to 1$, simple ageing occurs, whereas in the limit $\mu \to 0$, obviously, no effect of ageing is seen (also see Fielding *et al.* 2000). For a soft microgel paste, Cloitre *et al.* (2000) observed that when a vanishingly small stress is applied to the system, one obtains the limit $\mu = 1$, while in the limit of very large stresses, one recovers the system that does not age ($\mu = 0$) until the stress is removed. Furthermore, a strong stress field leading to plastic deformation, as in the present case, is known to erase the deformation history of the sample (Utz *et al.* 2000) and, also, it does not let the system age (as plateau viscosity does not change with time). Thus, the present observation that the minor differences in the rejuvenation step do not affect the long-term ageing behaviour (as long as a strong stress field is applied in the rejuvenation) is not surprising. Interestingly, Cloitre *et al.* (2000) have also reported similar observations for a microgel paste.

Figure 3 shows the evolution of the complex viscosity for a shear-rejuvenated laponite suspension for a range of molar concentrations of NaCl. It is evident that the systems with higher salt concentration are stiffer when compared at the same age. Furthermore, the complex viscosity shows a power-law type dependence on age ($\eta^* \sim t_{\mathrm{w}}^{x}$). The corresponding power-law exponent (x) is plotted against the molar concentration of Na^+ ions as an inset in the same figure. It can be seen that the complex viscosity shows a weaker dependence on age with an increase in the salt concentration. Pignon *et al.* (1997*b*) also observed that the storage and loss moduli of systems with a higher salt concentration are higher at the same age; however, they did not report the rate of increase of the moduli with age. We also carried out experiments with 2% laponite suspensions with 10^{-2} M ionic concentration, whose ageing behaviour is represented by open circles in figure 3. The latter sample shows a different ageing behaviour compared with the 3.5% samples. It should be noted that at a sufficiently higher age, the contribution of the viscous modulus to the complex viscosity is negligible, which makes G' vary with age in a similar fashion to the complex viscosity, as shown in figure 3.

In a non-ergodic state, owing to their disc-like shape and non-uniform charge distribution, laponite particles can be considered to be trapped in a cage of surrounding particles that can be represented by a potential energy well.

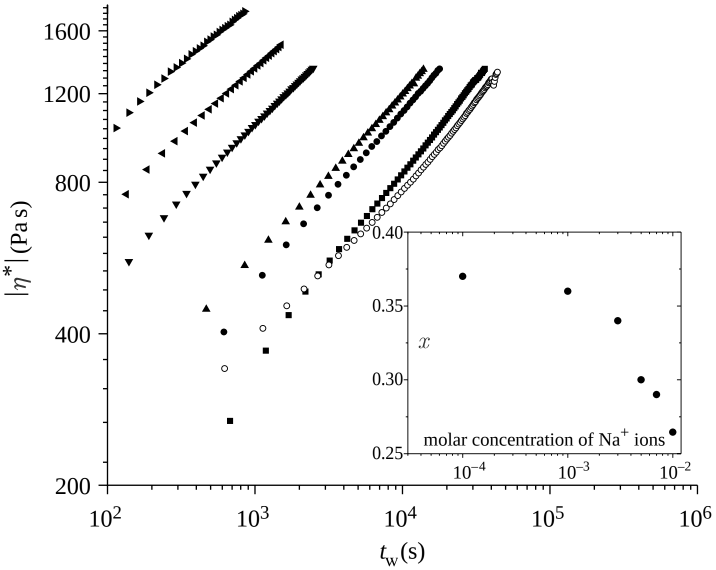

Figure 3. Evolution of complex viscosity with age after rejuvenation for aqueous laponite suspensions with different salt concentrations. Filled symbols, clay concentration 3.5% with different molarities, from top to bottom: 10^{-2}, 7×10^{-3}, 5×10^{-3}, 3×10^{-3}, 10^{-3} and 10^{-4} M. Open circles, 2% 10^{-2} M clay system. Inset shows dependence of power-law exponents x (for $\eta^* \sim t_w^x$) on molar concentration of Na$^+$ ions.

Distribution of such local energy minima is known as an energy landscape (Fielding *et al.* 2000). Although there is no global minimum, each laponite particle undergoes activated dynamics of structural rearrangements so that the system attains a lower energy state with age, making the system more elastic. An increase in the salt concentration decreases the electrostatic screening length associated with the laponite discs, changing the energy landscape and its evolution with age. It is generally believed that an increase in the salt concentration leads to the formation of a gel-like state, while for the system with no salt, a glass-like state is formed. The ageing dynamics shown in figure 3 essentially capture this, where an increase in the salt concentration changes the evolution of complex viscosity (elastic modulus) with age. Cocard *et al.* (2000) reported that the rate of gelation increases with ionic strength. However, if the increase in complex viscosity with age is considered as a signature of ageing (or gelation at higher ionic strength), we observe that after sufficient age, the rate of gelation decreases with the increase in ionic strength.

We carried out ageing experiments for all samples until the complex viscosity reached a predetermined value, typically between 300 and 1750 Pa s. After stopping the oscillatory test each time, a creep experiment was performed. Figure 4 shows a typical creep curve for a sample having a complex viscosity of 300 Pa s. In the initial period up to $O(1\ \mathrm{s})$, the system shows significant oscillations in strain that attenuate very quickly. Similar oscillations are also observed in the recovery experiments. Such behaviour is known to occur as a result of the viscoelastic character of the fluid coupled with the instrument inertia. Baravian & Quemada (1998) have analysed this so-called creep ringing behaviour

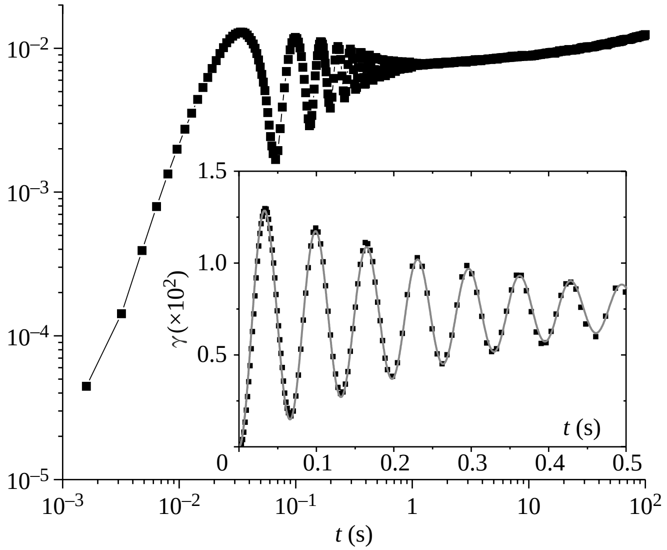

Figure 4. Typical creep behaviour of aqueous laponite suspension. At early times, damped oscillations in strain are observed. The line is a guide to the eye. The inset shows a fit of equation (3.3) to the experimental data. It can be seen that only a single mode fits the data well.

for various linear viscoelastic models. The essential features of this approach are recapitulated here. The application of Newton's second law of motion to a rheometer system leads to (Baravian & Quemada 1998)

$$a\ddot{\gamma} = \sigma_0 - \sigma, \tag{3.1}$$

where a is the moment of inertia of the mobile part; γ is the shear strain; and σ_0 and σ are the stresses corresponding to the applied and effective torques, respectively. The Maxwell–Jeffreys constitutive relation (mechanical model shown in figure 5), written as

$$(\eta_1 + \eta_2)\dot{\sigma} + G\sigma = \eta_1\eta_2\ddot{\gamma} + \eta_2 G\dot{\gamma}, \tag{3.2}$$

coupled with equation (3.1) can be solved analytically for the creep flow with a constant shear stress σ_0. The resultant shear strain γ is given by (Baravian & Quemada 1998)

$$\gamma(t) = \sigma_0\left\{\frac{t}{\eta_2} - B + \mathrm{e}^{-At}\left[B\cos\overline{\omega}t + \frac{A}{\overline{\omega}}\left(B - \frac{1}{A\eta_2}\right)\sin\overline{\omega}t\right]\right\}, \tag{3.3}$$

where $A = (aG + \eta_1\eta_2)/(2a(\eta_1+\eta_2))$; $B = ((a(\eta_1+\eta_2))/(\eta_2 G))((2A/\eta_2) - (1/a))$ and $\overline{\omega} = \sqrt{(\eta_2 G/a(\eta_1+\eta_2)) - A^2}$. It can be seen that for real values of $\overline{\omega}$, the shear strain undergoes damped oscillations in a creep experiment, as shown in figure 4. Furthermore, the damped oscillatory response attenuates quickly, which is followed by the usual creep behaviour.

The inset in figure 4 shows a fit of equation (3.3) to the damped oscillatory strain response plotted in figure 3 in the initial stages (up to 0.5 s). It can be seen that equation (3.3) provides an excellent fit to the oscillatory data, from which model parameters η_1, η_2 and G can be obtained at various ages of the sample.

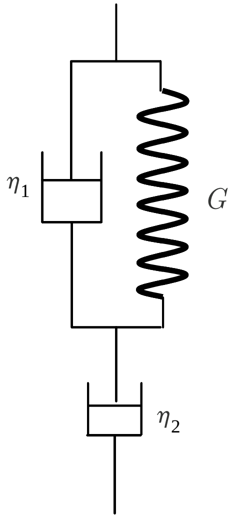

Figure 5. Schematic of a Maxwell–Jeffreys model.

The value of a is obtained by measuring the strain for the applied stress without any sample, as suggested by Coussot *et al.* (2006). Furthermore, similar to the findings of Coussot *et al.* (2006), the values of G and G' were seen to be very similar. Equation (3.3) was fitted to the experimental data using the Levenberg–Marquardt method for nonlinear least-squares fitting of the commercial software ORIGIN v. 7. It should be mentioned here that the fit was not particularly sensitive to the value of η_2 over several decades. This is not at all surprising since the experimental data used in the fit are limited only up to 0.5 s, over which the deformation is predominantly elastic in nature. In order to get the exact value of η_2, we made use of the data obtained from the oscillatory experiments. Findley *et al.* (1976) have discussed the oscillatory response of the Maxwell–Jeffreys model. If $p=(\eta_1+\eta_2)/G$ and $q=\eta_1\eta_2/G$, then the storage and loss moduli of the Maxwell–Jeffreys model are given by

$$G' = \frac{p\eta_2\omega^2 - q\omega^2}{p^2\omega^2+1} \quad \text{and} \quad G'' = \frac{pq\omega^3+\eta_2\omega}{p^2\omega^2+1}. \tag{3.4}$$

For the range of values of η_2 for which an excellent fit to the oscillatory behaviour is obtained, we observed that $\eta_1 \ll \eta_2$, $G^2/\eta_2 \gg \eta_1\omega^2$, $a/\eta_2^2 \ll 1/G$ and $G/\eta_2 \ll \eta_1/a$. This in turn leads to considerable simplifications of the above expressions of the elastic and viscous moduli as follows:

$$G' \approx G \quad \text{and} \quad G'' \approx \frac{G^2}{\eta_2\omega}. \tag{3.5}$$

Thus, the values of η_2 as a function of age can be easily obtained from the oscillatory data via equation (3.5). Thus, following the above-mentioned procedure, all the model parameters of the Maxwell–Jeffreys model can be estimated with respect to age. It should be noted that we carry out the oscillatory experiments at a frequency of 0.1 Hz. If the experiments had been

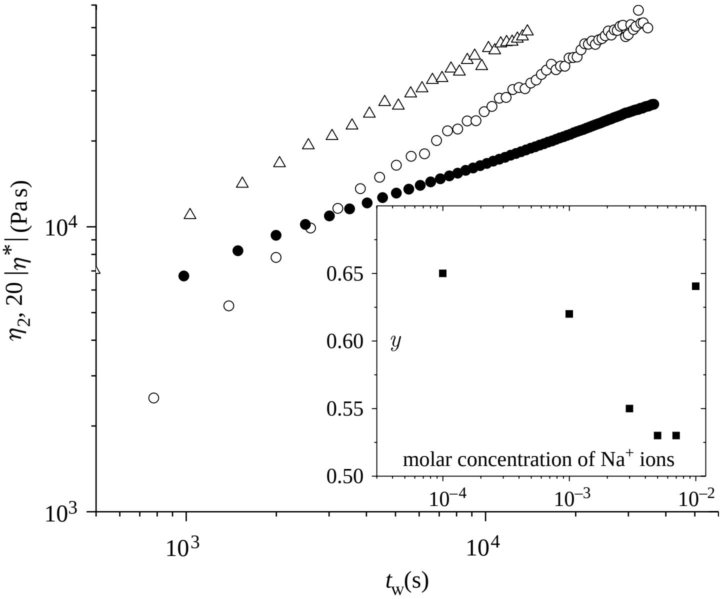

Figure 6. Evolution of η_2 with age after rejuvenation for aqueous laponite suspensions for two salt concentrations. Open circles, 10^{-4} M; open triangles, 3×10^{-3} M. Filled circles show corresponding evolution of complex viscosity for the system with no salt (10^{-4} M). The inset shows the dependence of the power-law exponents y (for $\eta_2 \sim t_w^y$) on molar concentration of Na$^+$ ions.

performed at very high frequency such that $G^2/\eta_2 \ll \eta_1\omega^2$, we would have recovered a Kelvin–Voigt response (Maxwell–Jeffrey model minus dashpot) from the oscillatory behaviour. However, performing experiments at high frequencies may not be always possible with a rheometer due to instabilities that occur due to inertia effects (Marin 1988). The Kelvin–Voigt response can also be recovered in the limit of $\eta_2 \rightarrow \infty$. However, in the present case, we get a response expressed by equation (3.5), which is different to the Kelvin–Voigt response, as η_2 is not large enough and the time scale of deformation is comparatively large (i.e. ω is small). Thus, the present experimental scheme gives us an advantage in order to estimate η_2 from oscillatory experiments, which otherwise is very difficult to measure due to scattering in steady shear data at low stresses and rejuvenation at high stresses.

Figure 6 shows η_2 for various salt concentrations as a function of age. Included in this figure are also the results for the system without any salt. It can be seen that η_2 increases more rapidly with age and is significantly larger in magnitude than the complex viscosity. The inset of figure 6 shows the power-law exponent for the dependence of η_2 on age plotted against molar concentration of Na$^+$ ions. It can be seen that the dependence of η_2 on age becomes weaker with increasing salt concentration; this trend is similar to that of the dependence of the complex viscosity on age. However, for the molar concentration 10^{-2} M, the exponent shows a sudden increase. This may be due to the fact that the 3.5% system flocculates at about this molar concentration of the salt (Mourchid *et al.* 1995*a*; Tanaka *et al.* 2004; Mongondry *et al.* 2005; Ruzicka *et al.* 2006).

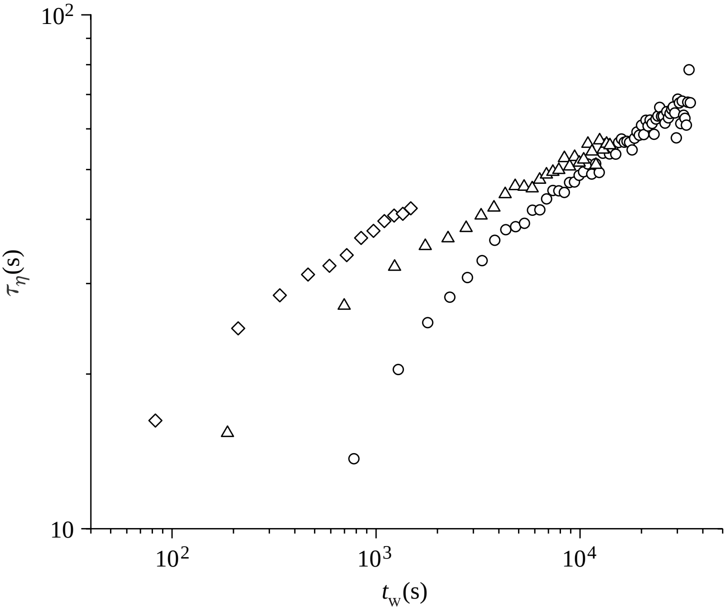

Figure 7. Variation of dominating rheological time scale τ_η as a function of age for various salt concentrations. Open circles, 10^{-4} M; open triangles, 3×10^{-3} M; open diamonds, 7×10^{-3} M.

The Maxwell–Jeffreys constitutive relation has two time scales associated with it. The slow time scale is associated with the shear viscosity η_2 and shear modulus G, while the second time scale, also known as the retardation time scale is linked with the viscosity η_1 and shear modulus G. The former time scale is given by

$$\tau_\eta = \eta_2/G. \tag{3.6}$$

Figure 7 shows the dependence of this time scale on age for a range of values of salt concentration. It is readily seen that the value of τ_η is significantly smaller than the age of the system. In the literature, it is believed that τ_η has the same magnitude as the α relaxation mode of the system. However, the present results vary from this trend, as not only its magnitude is significantly smaller than its age, but its dependence on age is also weaker than the linear dependence reported in the literature.

The second characteristic time of the system, the retardation time, can be obtained from η_1 and G, and is defined as (Harrison 1976; Barnes *et al.* 1989)

$$\tau_r = \eta_1/G. \tag{3.7}$$

The retardation time controls the rate of growth of strain following the imposition of the stress (Barnes *et al.* 1989). As the Maxwell–Jeffreys model depicted in figure 5 suggests, it is essentially related to the viscous environment (or friction) associated with the elastic component of the system. As discussed previously, in the non-ergodic state, individual charged laponite particles can be considered to be trapped in a potential energy well of surrounding particles. Such entrapment of particles is essentially responsible for the elasticity of such an

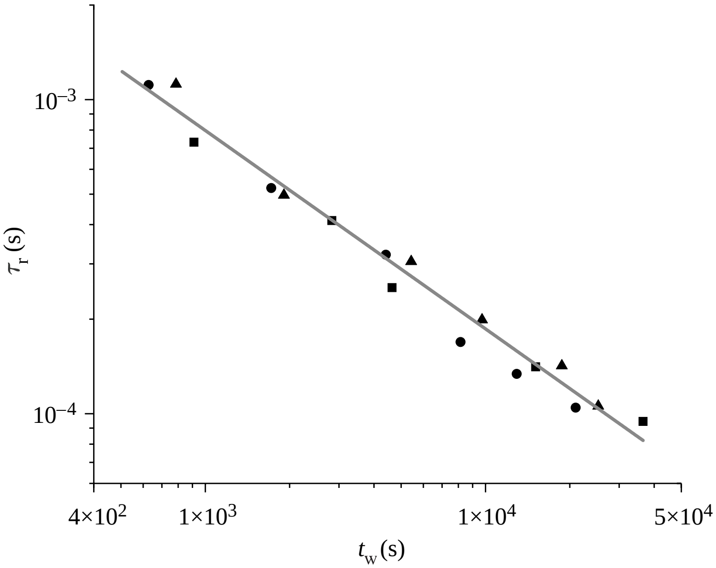

Figure 8. Dependence of retardation time τ_r on age at various stresses for the 3.5% 10^{-4} M sample. Filled circles, 0.5 Pa; filled squares, 1.5 Pa; filled triangles, 3.0 Pa.

ageing suspension. When a step stress is applied to the system, the particles change their position by working against the potential energy field. The dissipative environment surrounding the particles resists any sudden change in the position and retards this process. Thus, the retardation time denotes the contribution of friction while the system is undergoing elastic deformation. The greater the friction that particles encounter upon the application of stress, the greater is the retardation time. A spectrum of retardation times is represented by a series combination of several Kelvin–Voigt elements (Maxwell–Jeffreys mechanical model minus the dashpot; Harrison 1976, Barnes *et al.* 1989). However, for the present system, only a single Kelvin–Voigt element fits the oscillatory data well, thereby suggesting that the retardation time of the system is nearly monodispersed.

Figure 8 shows the dependence of τ_r on age for the 3.5% 10^{-4} M sample for various creep stress levels, namely 0.5, 1.5 and 3 Pa. It can be seen that the retardation time decreases with respect to age. This result is particularly significant, as it suggests a reduction in friction in the neighbourhood of arrested particles, showing a decrease in resistance to elastic deformation with age. Furthermore, the dependence of the retardation time on age ($\tau_r \sim t_w^{-0.6}$) is independent of the applied stress. We also confirm this result by carrying out additional creep tests on suspensions having different molarity at various stresses. We believe that, since the response time of the damped oscillations is $O(1\,\mathrm{s})$, stress may not be able to influence the fluid behaviour, as deformation is essentially elastic over this time scale, thereby showing the retardation time to be independent of the applied stress.

An evolution of the energy landscape giving more weightage to the lower energy states with age is responsible for an increase in the elasticity of the system, as shown in figure 3. This inherent elastic character of the system, coupled with the inertia of the system, is responsible for an oscillatory response

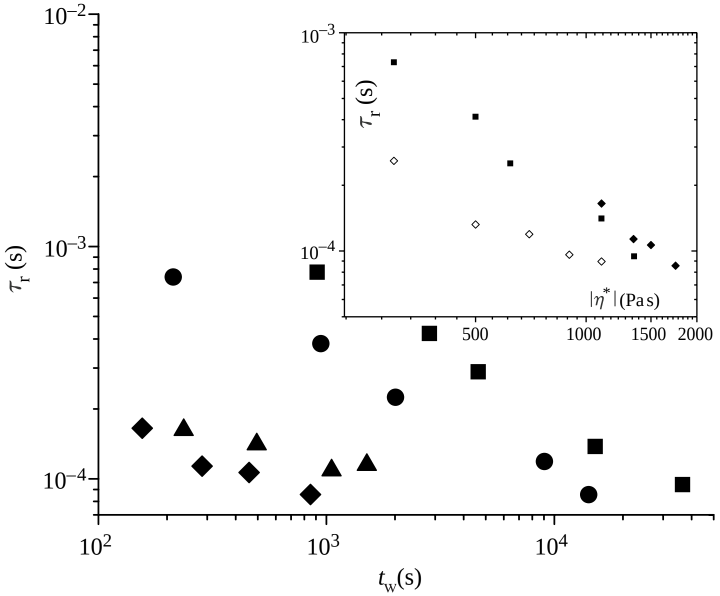

Figure 9. Dependence of retardation time τ_r on age. The inset shows dependence of retardation time on complex viscosity. Open symbols in the inset, 2% 10^{-2} M suspension; filled squares, 10^{-4} M; filled circles, 3×10^{-3} M; filled triangles, 7×10^{-3} M; filled diamonds, 10^{-2} M.

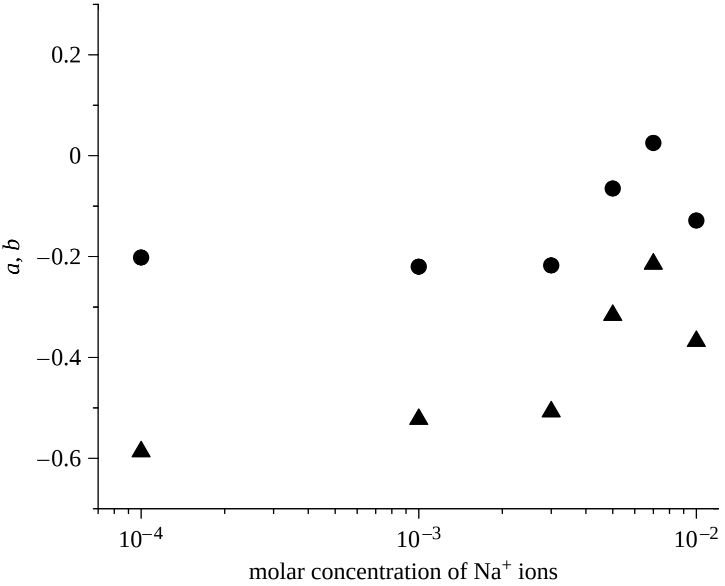

Figure 10. Dependence of power-law exponents a (filled circle, $\eta_1 \sim t_w^a$) and b (filled triangles, $\tau_r \sim t_w^b$) on molar concentration of Na^+ ions.

to the applied step stress, which is damped by the dissipative environment (friction) surrounding the particles leading to the overall damped response. Figure 9 shows the dependence of τ_r on age for a range of salt concentrations. In figure 10, power-law exponent b for $\tau_{\rm r} \sim t_{\rm w}^{b}$ is plotted with respect to the ionic concentration. Both these figures show that $\tau_{\rm r}$ significantly decreases with age at low salt concentrations. Similar to the trend observed for η_2, the power-law exponent for ionic concentration 10^{-2} M shows a sudden change in the behaviour, which may be due to flocculation.

The inset of figure 9 shows $\tau_{\rm r}$ plotted against complex viscosity for two systems having 3.5% laponite, along with a system having 2% laponite and molarity 10^{-2} M, in order to get a feel of the dependence and magnitudes of the retardation time on concentration at the same level of complex viscosity. The values of $\tau_{\rm r}$ for the 3.5% suspensions at other salt concentrations were found to be of the same order of magnitude as the two 3.5% systems shown in the inset of figure 9; hence, these data are not included here to avoid overcrowding. It can be seen that the value of $\tau_{\rm r}$ for the 2% system is significantly smaller than that of the 3.5% system. This suggests that the value of η_1 of the 2% system must also be smaller than that of the 3.5% systems at a constant value of G (or η^*). This implies that a decrease in laponite concentration causes a decrease in η_1. This observation further strengthens our proposal that η_1 may be associated with a dissipative environment or friction and increases with an increase in the laponite concentration.

Light scattering studies on ageing laponite suspensions generally characterize fast and slow time-scale dependence on age (Abou *et al.* 2001; Bellour *et al.* 2003; Kaloun *et al.* 2005; Tanaka *et al.* 2005; Schosseler *et al.* 2006). In the light scattering experiments, autocorrelation function shows two-stage decay. A normalized autocorrelation function is then fitted by an empirical equation having a sum of an exponential and a stretched exponential function to yield α and β relaxation time scales (Abou *et al.* 2001). The fast or β time scale is considered to be related to the rattling motion of the trapped entity, and is observed to be independent of age (Tanaka *et al.* 2005; Schosseler *et al.* 2006). It is however worthwhile to add here that the retardation time $\tau_{\rm r}$ is not the same as the β mode, as the latter remains constant with age. On the other hand, the slow or α time scale represents the time scale of cage diffusion, and is observed to increase linearly with age under static conditions (Knaebel *et al.* 2000; Schosseler *et al.* 2006). It is interesting to note that, although the α time scale increases with age due to the deepening of the energy well, the retardation time actually decreases suggesting a decrease in the resistance to elastic deformation. The activated dynamics that jammed particles undergo might be responsible for positioning them in the cooperative environment of the cage such that resistance to elastic deformation decreases, indicating a decrease in local friction surrounding the particles. Thus the retardation time, as used in the present context, provides an additional vantage point to study the phenomenon of ageing in such systems.

In order to gain further insights about the dependence of η_1, we have plotted η_1 with age for various salt concentrations in figure 11. Figure 10 shows the corresponding dependence of power-law exponent a for $\eta_1 \sim t_{\rm w}^{a}$ with respect to the ionic concentration. In general, it can be seen that the dependence of η_1 on age shows a similar trend to that of $\tau_{\rm r}$. It should be noted that, while discussing retardation behaviour, we are concentrating on creep time up to $O(1\ {\rm s})$, thereby focusing only on the elastic deformation of an ageing laponite suspension. The frictional contribution, represented by a dashpot with viscosity η_1 in figure 5, contributes towards resisting elastic deformation of the system. Figure 10 also

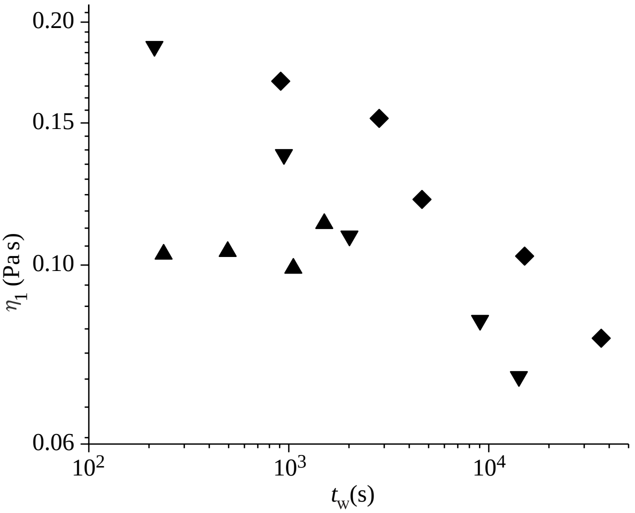

Figure 11. Evolution of η_1 as a function of age for various salt concentrations. Filled diamonds, 10^{-4} M; filled down triangles, 3×10^{-3} M; filled triangles, 7×10^{-3} M.

shows that η_1 is a decreasing function of age up to a molar concentration of Na^+ ions of 3×10^{-3} M. Beyond that this dependence weakens significantly. A decrease in η_1 with age suggests a reduction in frictional contribution that resists elastic deformation of the system. We believe that this frictional contribution represented by η_1 arises from the effective viscosity of the medium surrounding the laponite particles, which seems to be decreasing with age as the laponite particles undergo activated dynamics and progressively attain lower energy. However, this frictional contribution is different to the overall resistance the system offers to deformation at a larger time scale represented by η_2, which is observed to be strongly increasing with age, as shown in figure 6. This result is particularly very significant since ageing is known to enhance resistance to translational diffusion; however, present results suggest that this is accompanied by a reduction in friction in the neighbourhood of the arrested entity.

It is generally believed that in the absence of any salt, repulsive interactions prevail among laponite particles, which lead to the formation of colloidal Wigner glass (Mourchid *et al.* 1995*a*,*b*; Tanaka *et al.* 2004; Schosseler *et al.* 2006). In the glassy state, the system is in a non-ergodic regime due to structural arrest caused by strong repulsive interactions. As the concentration of Na^+ ions increases, it gradually screens electrostatic repulsion and, at sufficiently high concentrations of Na^+ ions, attractive interactions prevail. This causes a fractal network of laponite particles that spans the whole space leading to a gel state (Pignon *et al.* 1996, 1997*a*,*b*; Nicolai & Cocard 2001). Figure 12 shows a schematic of a glassy and gel state, as postulated by Tanaka *et al.* (2004). The critical salt concentration delineating the boundary between the glass and gel states is, however, far from obvious and as such is a matter of debate (Mourchid *et al.* 1995*a*; Tanaka *et al.* 2004; Mongondry *et al.* 2005; Ruzicka *et al.* 2006, 2007). Accordingly, it is obvious that the presence of Na^+ ions alters the energy landscape significantly and, as a consequence, the activated dynamics that cause ageing in the non-ergodic state.

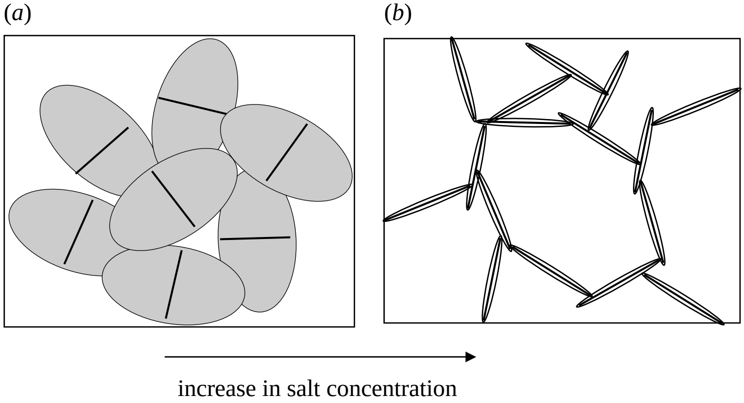

Figure 12. Schematic of arrested states. (*a*) At low ionic concentration, electrostatic repulsion between laponite particles leads to a glassy state. (*b*) At high ionic concentration, cations screen the negative charge, which leads to a gel state.

In a light scattering study of laponite suspension, Nicolai & Cocard (2001) observed that for ionic concentrations above 10^{-3} M, the characteristic length scale of the network (gel), the correlation length, increases with age. They further observed that correlation length increases with ionic strength and decreases with concentration of laponite. However, at lower ionic concentration, the static structure factor was observed to decrease with age indicating an increase in the repulsive interactions (Tanaka *et al.* 2004). A very recent study of Brownian dynamics simulations by Mossa *et al.* (2007) suggested that ageing dynamics strongly affect orientational degree of freedom, which relaxes over the time scale of the translational modes. The rheological study described in this work gives further insights into the ageing dynamics. We observe that, as repulsive interactions decrease gradually (with an increase in the salt concentration), the rate of decrease of the retardation time with age, which signifies resistance to elastic deformation or friction localized in the neighbourhood of the particle, becomes weak. Furthermore, not just retardation time but all the other characteristics of the system, including complex viscosity, show weaker evolution with respect to age with an increase in the salt concentration. This observation indicates that activated dynamics are faster in a glass state than in a gel state.

The present work clearly distinguishes between ageing in a glass and gel. In structural glasses, ageing leads to densification by causing a greater order in the molecular arrangement. In colloidal glasses, although density remains constant, ageing is expected to cause progressive ordering, which should lead to more relative space between the constituents that may cause a reduction in resistance to elastic deformation. We propose that as colloidal glass ages it leads to a more ordered state with respect to age, although complete crystallization may not be possible and thus demonstrates the observed behaviour. However, as we increase the salt concentration, the state of the suspension changes to a gel. Since a gel state is inherently different in structure (fractal network) to that of a glass (disordered), ageing in the gel does not lead to ordering, and we observe a weaker dependence of retardation time on age with an increase in the salt concentration. Therefore, the present work differentiates between a glass and a gel by their ageing behaviour such that a glass forms a greater ordered structure upon ageing, which is not likely in the case of a gel. This is a very significant observation that elucidates an important difference between a glassy state compared with a gel state, a matter that has been debated in the literature at great length. We believe that various results described in the present work provide significant additional insight into the ageing dynamics of colloidal glasses and gels, which may provide stimuli for further studies on soft glassy materials.

4. Summary

Ageing dynamics of aqueous laponite suspensions at various salt concentrations are studied using rheological tools by employing a well-defined rejuvenation procedure. It is observed that for large values of the rejuvenating stress, minor differences in the rejuvenation procedure do not affect the ageing behaviour of laponite suspensions. Subsequent ageing experiments are carried out until a predetermined complex viscosity value is reached and then creep experiments are performed. In general, we observe that shear viscosity is significantly higher in magnitude than the complex viscosity and increases very rapidly. In creep experiments, soft solids of laponite show oscillations in strain that attenuate over a time period $O(1\ \mathrm{s})$ due to the coupling of the viscoelasticity of the sample with the instrument inertia. A single mode Maxwell–Jeffreys model coupled with inertia gives an excellent fit to the damped oscillation. The characteristic time scale of the Kelvin–Voigt element of the Maxwell–Jeffreys model, also known as the retardation time ($\tau_\mathrm{r} = \eta_1/G$), is seen to be independent of the applied stress; however, it decreases with the age of the sample. Furthermore, the rate of decrease of τ_r becomes weaker with an increase in the salt concentration. The 2% laponite shows significantly lower values of τ_r compared with the 3.5% suspensions. In the present context, the retardation time is associated with the time required for a transient to attenuate while approaching a steady state, and it represents a frictional contribution of the viscous medium surrounding the particles that resist elastic deformation of the system. Notably, these results show that when the resistance to translational diffusion of the arrested entities increases with age, at a local level, the friction actually decreases. This decrease becomes weaker with an increase in the salt concentration, which is known to change the system from a glass state to a gel state. In addition, we observe that the ageing dynamics in the glassy state are faster than those in the gel state. Simple analogy of colloidal glasses with molecular glasses suggests that ageing should induce greater ordering, which provides more space for the constituents of the glass, resulting in lesser resistance to elastic deformation. However, as we increase the salt concentration, the state of the suspension changes to a gel. Since a gel comprises a fractal network, ageing in the gel does not lead to an ordered structure and we observe a weaker dependence of retardation time on age with the increase in the salt concentration. This study clearly shows that the use of rheological tools can certainly provide useful insights, thereby leading to a better understanding of the ageing behaviour in soft glassy materials.

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