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Signatures of structural recovery in colloidal glasses

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ABSTRACT

Colloidal systems near to the glass concentration are often taken as models for molecular glass formers. Yet, one of the most important aspects of the dynamics of molecular glasses -- structural recovery, has not been fully elucidated in colloidal systems. We take advantage of a thermosensitive PNIPAAm colloidal suspension to study the structural recovery after concentration jumps in the glass concentration range by using diffusive wave spectroscopy. The three classical aging signatures observed in molecular glasses: intrinsic isotherms, asymmetry of approach, and memory effect, are investigated with this colloidal suspension and the results are compared with those typical of molecular glasses. We find that: 1) for the intrinsic isotherms, unlike molecular glasses, the colloid shows dramatic changes in relaxation time at equilibrium while the times required to reach the equilibrium state are nearly independent of the concentration; 2) for the asymmetry of approach, we find a similar nonlinearity to that observed in the molecular glasses; 3) for the memory experiment, while memory effect is seen in the colloid, the response is qualitatively different from that in molecular glasses.

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There is significant interest in the aging behavior of both colloidal suspensions [1-4] and molecular glasses [5-7] around the glass transition. In the case of the former, aging is generally studied after shear melting at a constant concentration and measured by using techniques such as rheology [3], diffusive wave spectroscopy [8, 9], and particle tracking microscopy [4, 10]. On the other hand, molecular glasses are typically investigated using temperature jumps through the glass temperature. As a result, the relationship between the behavior of molecular glasses and colloidal systems remains elusive, though the colloidal system is often taken as a simple model for molecular glasses. In the present work we use diffusive wave spectroscopy (DWS) to investigate the aging dynamics of a colloidal dispersion made of thermoresponsive particles of poly(N-isopropylacrylamide) [PNIPAAm] [11, 12] in concentration jump histories that, in principle, should mimic the temperature jump histories commonly used to study structural recovery and physical aging in molecular glasses.

The aging signatures of molecular glasses: (1) intrinsic isotherms; (2) asymmetry of approach; and (3) memory effect, were catalogued by Kovacs[4] by means of experiments characterized by a temperature-jump from the equilibrium state to a temperature below the nominal glass transition temperature T_g . In the intrinsic isotherm experiment, Kovacs decreased the temperature of the sample from a single starting temperature $T_0 \approx T_g$ to a series of final temperatures below T_g . The time for the volume to reach equilibrium was found to increase rapidly as temperature decreases. The asymmetry of approach experiment involves comparison of two temperature change steps with the same magnitude: a down-jump from $T_1 + \Delta$ to T_1 and an up-jump from $T_1 - \Delta$ to T_1 . The profile of the volume recovery curves is not mirror-symmetric but is highly asymmetrical and the reason for this is the dependence of the relaxation times on the volume departure from equilibrium δ (defined below), i.e. when $\delta > 0$, the recovery is more rapid than when $\delta < 0$. In the memory experiments, the sample is first subjected to a temperature down-jump from T_0 to T_i , where the sample recovers partially towards equilibrium. After this partial recovery step, the temperature is increased to T_1 ($T_i < T_1 < T_g$). In this case, the material ‘remembers’ the prior history and the volume increases to a maximum value before decreasing and merging to the curve obtained when jumping directly from T_0 to T_1 . The existence of the memory provides evidence for a non-exponential relaxation response for the structural recovery

as well as its history dependence. These aging signatures are seen in molecular glasses, not only for thermal histories, but also for concentration histories [13], i.e., jumps in humidity.

Colloids at high concentration exhibit similar behaviors to molecular glasses [14], viz. the apparent divergence of relaxation time τ with increasing volume fraction ϕ [15]. Dynamical heterogeneity and cooperativity in colloids are also considered as glass-like properties [9]. Jamming [16] brings a unifying view between colloidal and conventional glasses that increasing ϕ in a colloid is equivalent to decreasing temperature (i.e., decreasing volume) in a conventional glass. The relevant aging signatures in glassy systems involve a rapid change of a control parameter, e.g., temperature[4, 6] or humidity[13] that drives the glass transition. Colloidal samples are generally studied in an iso-concentration state. Rapid changes in concentration are difficult to attain and aging in colloids has, consequently, not been investigated in the same ways as in molecular glasses.

The samples we used in the present work were dispersions of thermosensitive PNIPAAm particles in water with total volume $\sim 2.9\text{cm}^3$ (1.2cm x 1.2cm x 2cm). The PNIPAAm particles exhibit extremely rapid temperature-induced swell-shrink responses [11, 12, 17]. By controlling the temperature, the diameter of the particle can be controlled and as a result, rapid volume fraction adjustment can be achieved. Here we take volume fraction as $\phi = \phi_m (d / d_c)^3$ where ϕ_m is the mass fraction, d_c is the diameter of a completely de-swelled particle and d the diameter of the particles. The diameter of our PNIPAAm particles decreases from 350 to 150 nm when temperature is raised from 24 to 36°C which is similar to Wu et.al's thermally responsive PNIPAAm microgel colloids [18]. We worked here with a slightly polydisperse ($2\sigma=10\%$) sample to avoid potential crystallization that normally occurs for monodisperse systems. In the present work, the temperature jumps were non-ideal and it took approximately 100-200s to stabilize the temperature depending on the magnitude of the temperature change. The temperature was stable to $\pm 0.01^\circ\text{C}$.

The method we used to monitor the changing glassy structure in the present investigation was multi-speckle diffusive wave spectroscopy in backscattering geometry [19]. In the experiment, the sample was illuminated using a 633 nm laser and the backscattered light was collected onto a CCD camera at 90 frames/second. The ensemble average auto-correlation function $g_2(t)$ is

obtained from:

$$g_2(t) = \langle I_i(0)I_i(t) \rangle / \{ \langle I_i(0) \rangle \langle I_i(t) \rangle \} \quad (1)$$

where I_i refers to the intensity of backscattering light at the i^{th} pixel, which is a function of time. The physical meaning of g_2 is the similarity between two frames by comparing the intensity of the same pixel at different time and averaging this intensity difference over all the pixels in the frame.

For a molecular glass, when temperature is cooled below T_g , it enters a non-equilibrium state, where the volume of material decreases continuously as a function of aging time t_w until reaching the equilibrium state. Kovacs defined the volume departure from equilibrium [4] as

$\delta(t) = (V(t) - V_{\infty})/V_{\infty}$, where $V(t)$ is the specific volume at time t and V_{∞} is the equilibrium volume at a given experimental temperature. In the present experiment, the volume during aging does not change. Therefore we introduce a structural parameter we refer to as the fictive volume, V_F which is similar in concept to Tool's [20] fictive temperature, T_F and we define it and its departure from equilibrium subsequently.

Fig. 1a shows g_2 vs. t at different aging time t_w for a typical run in a temperature down-jump experiment. As t_w increases, the curves move toward the right due to aging of the system. When $t_w > 1000$ s the curves overlap with each other—consistent with the system reaching equilibrium. The g_2 curves of Fig. 1a all have the same shape and a master curve was obtained (shown in Fig. 1b) by shifting the curves along the time axis. This result implies that the time-aging time-superposition is valid here [5]. We define the relaxation time $\tau_{1/2}$ as the time needed for g_2 to decay to its half value and for each g_2 vs. t , a relaxation time can be extracted at a specific aging time. The changes in relaxation time with t_w are similar to the changes in time-aging time shift factors used to create the master curve of Fig. 1b from the data of Fig. 1a.

Fig. 2a shows the evolution of the relaxation time as a function of t_w at different temperatures. For all of the relaxation curves, relaxation time increases initially and reaches a 'plateau' at large t_w , from which the values of equilibrium relaxation time are obtained. (We remark that the relaxation time in Fig. 2a may not level off for the lowest temperature systems even at the largest aging times. This interesting phenomenon might be worth further investigation but the rate of change is slow enough that we consider it as uncertainty in the experiments.) From the data of

Fig.2a, the relationship between equilibrium relaxation time and temperature was obtained and is depicted in Fig.2b. The figure shows a rapid increase of relaxation time with decreasing temperature (increasing concentration), consistent with glass-like behavior, and expected for this glass-forming system. We note that in the “power-law” region of the curves in Fig. 2a for the biggest temperature jumps the slope of the $\tau_{1/2}$ vs g_2 curves is greater than unity (≈ 1.5), which has been found in other instances for the aging response of $g_2(t)$ [21], but is more commonly found to be close to unity for, e.g., viscoelastic response and $g_1(t)$ for aging colloids and was found for many molecular glasses in the aging studies of Struik[5].

In order to construct a similar parameter to the volume departure from equilibrium in a molecular glass, we introduce the fictive volume ($V_F = 1/\phi_{eff}$) where ϕ_{eff} is the (effective volume fraction) and these parameters are conceptually similar to Tool’s fictive temperature conceptually[20]. At each temperature, then, there is a specific diameter of the PNIPAAm particle and a corresponding specific volume fraction for the colloidal suspension. Therefore, the equilibrium relaxation time vs. temperature curve (Fig.2b) can be transformed into an equilibrium relaxation time vs. fictive volume curve. By interpolating the relaxation time in Fig.2a onto the equilibrium relaxation time vs. fictive volume curve, we obtain the value of the fictive volume corresponding to each relaxation time during the aging experiment. Similar to the equation used to describe volume departure from equilibrium for a molecular glass [4], we use

$$\delta(t) = \frac{(1/\phi_{eff} - 1/\phi_{eq})}{(1/\phi_{eq})} = \frac{V_F - V_{eq}}{V_{eq}}$$

to describe the fictive volume departure from equilibrium for the colloidal suspension. The same batch of sample was used in all of our experiments and the systematic errors for V_F and V_{eq} should be the same, therefore δ would be reasonable within the experimental range. As in the case of the molecular glass, δ tends toward zero for colloidal suspension when t increases to a large value. Here we employ similar temperature change histories to those Kovacs used in his investigation of molecular glass and the departure from equilibrium δ , as a function of aging time is compared between colloidal and molecular glasses.

For the intrinsic isotherm experiment, the temperature of the colloidal suspension was decreased from 32°C to several different final temperatures between 31.8°C and 31.3°C with corresponding fictive volumes between 4.1 and 3.6. From Fig.3, it can be seen that for both colloidal and molecular glasses, a lower final temperature results in a larger volume change.

However, we also see that the time required for the colloidal suspension to reach equilibrium for the family of curves shown is insensitive to temperature while for the molecular glass it is a strong function of temperature. This is in spite of the fact that the equilibrium values of $\tau_{1/2}$ are strong functions of temperature. Also the magnitude of the volume (fictive) change for the colloid is much larger than the actual volume change for the molecular glass.

In the asymmetry of approach experiment, the final temperature of test was 31.5 °C corresponding to a volume fraction in equilibrium of $\phi_{\infty} = 0.264$. The concentration up-jump was performed from 31.3°C, corresponding to $\phi_{\infty} = 0.278$ and the down-jump was performed from 31.7 °C, corresponding to $\phi_{\infty} = 0.251$. Fig.4 shows the comparison of the asymmetry-of-approach experiment for colloidal and molecular glasses. The upper curve in Fig.4a is for the down-jump condition and the lower one for the up-jump. The asymmetry of these two curves can be observed, especially the fact that in the up-jump experiment the magnitude of the departure from equilibrium is larger than for the down-jump experiment, though there seems to be less of an asymmetry than in the case of the molecular glass depicted in Figure 4b. The comparatively noisy result for the present colloidal experiments is due to the extreme sensitivity of our particle to even the small temperature fluctuations in our experiments. We are now in the process of synthesizing core/corona particles that should have a lower temperature sensitivity, hence, presumably reducing the noise in the data.

The so-called memory experiment is a two-step history in which temperature is reduced and the material allowed to partially recover after the first step and then the temperature is jumped to a point close to where the initial departure from equilibrium δ_0 is close to zero. The structural recovery response is followed after the second step in temperature. Fig. 5 shows the time response of δ in a memory experiment for which the sample was partially aged at 31.2°C for 150s and then jumped to 31.5°C (black curve). The red curve is the direct jump (intrinsic isotherm) from 32°C to 31.5°C. Compared with the intrinsic isotherm curve (red), volume change in the structural memory experiment is much smaller but the insert in Fig.5a shows a clear peak. This experiment is the first to show the existence of a memory effect in the structural recovery for a colloidal system. The memory effect is thought to be caused by the non-exponential relaxation and history dependent response of the structural recovery [4, 22]. One aspect different from the molecular glass is that although we carried out experiments with

different partial recovery temperatures and the memory effect peak was observed, we observed no multiple memory effect peaks for the colloidal system, such as those seen in Fig. 5b for the molecular glass.

To summarize, a series of temperature-jump experiments was performed using suspensions of thermo-responsive PNIPAAm particles to investigate the aging response of colloidal glasses under conditions similar to those used in temperature-jumps in molecular glasses. Diffusing wave spectroscopy was used to measure dynamics in histories equivalent to intrinsic isotherms, asymmetry of approach and Kovacs memory experiments. The three signatures of aging in molecular glasses catalogued by Kovacs [4] were also found for the colloidal system. The nature of the responses in the colloid is different qualitatively from those of the molecular glasses. The intrinsic isotherms, while showing dramatically different equilibrium relaxation times, seem to age into equilibrium at times that are at best weakly dependent on the temperature, unlike the case of the molecular glasses that exhibit strongly growing time-scales for both the relaxation time and the structural recovery time. The non-linear result of asymmetry of approach experiments in the colloidal dispersion is similar in character to that observed in molecular glasses. The viscoelastic memory effect is also observed in the colloidal suspension although the multiple peaks that occur for partial recovery at different temperatures exhibited in molecular glasses are not obtained in the colloidal system.

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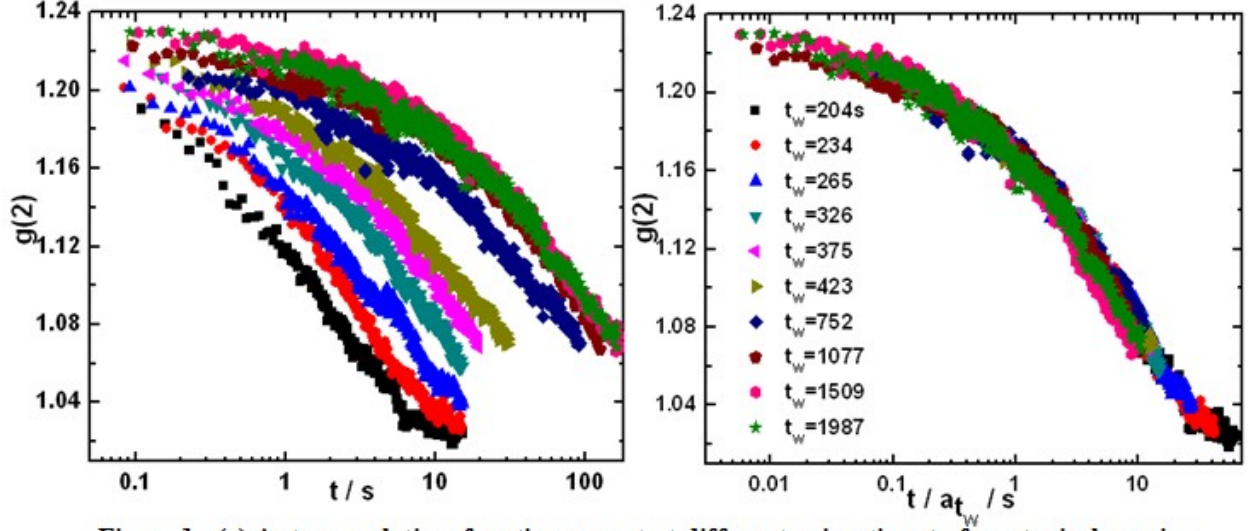


Figure 1. (a) Auto-correlation function g_2 vs. t at different aging time t_w for a typical run in a temperature down-jump from 32°C to 31.3°C. (b) Master curve of g_2 vs. t/a_{t_w} from time-aging time superposition.

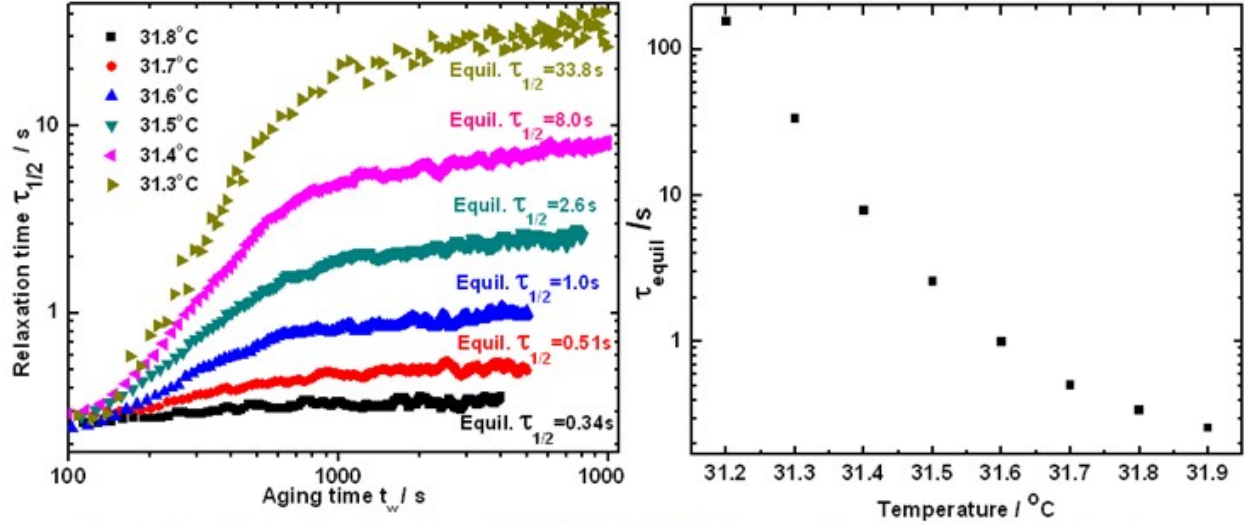


Figure 2. (a) Relaxation time for a PNIPAAm colloidal suspension as function of aging time at different temperature after temperature down jump from 32°C (b) Equilibrium relaxation time vs. temperature, consistent with glass-like behavior

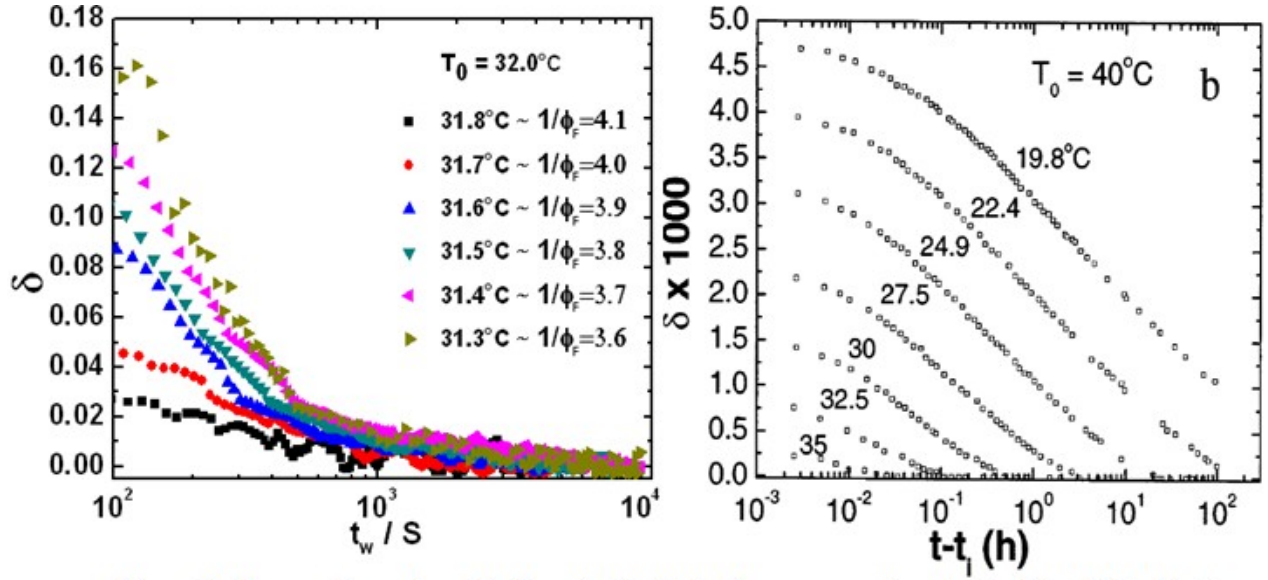


Figure 3. Comparison of results from intrinsic isotherms experiments for (a) colloid (start temperature $32^\circ C$); (b) molecular glass (start temperature $40^\circ C$) (Data from Kovacs [5], figure from Zheng and McKenna [13])

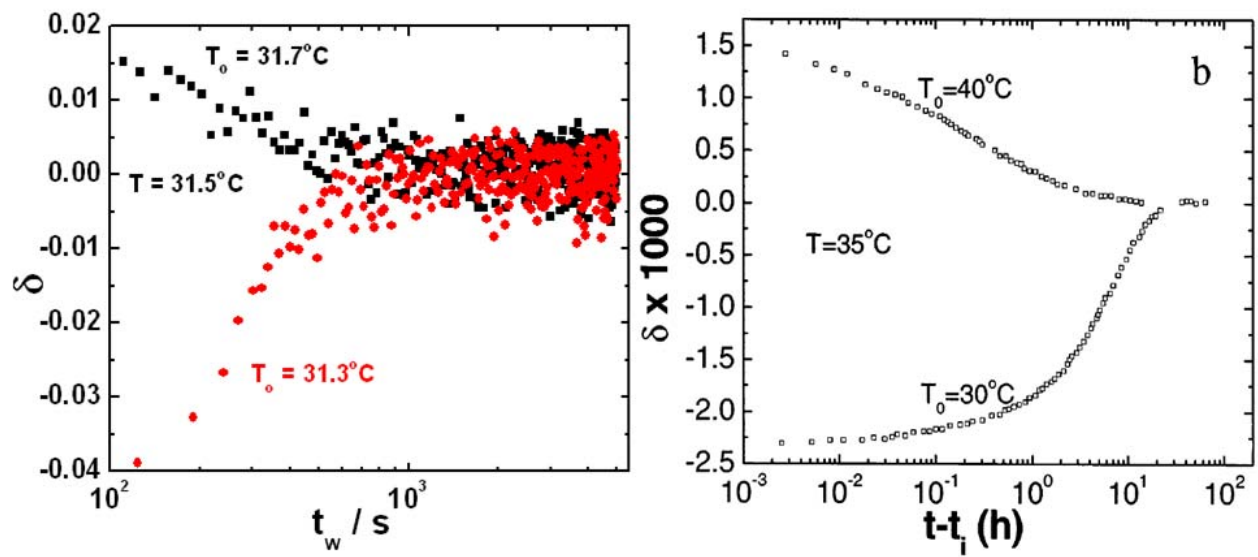


Figure 4. Comparison of the asymmetry of approach experiment results for (a) colloid; (b) molecular glass (data from Kovacs [4], figure from Zheng and McKenna [12]).

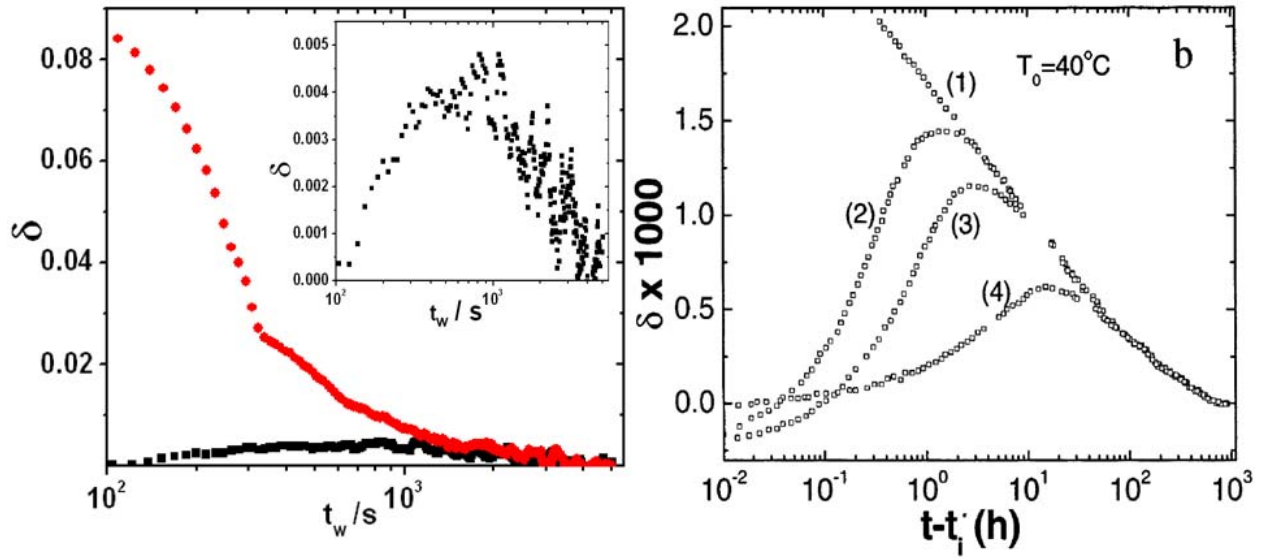


Figure 5 . Comparison of the memory effect experiment results for (a) colloid, $T_0=32^\circ\text{C}$, Waiting time =150s, $T_{\text{partial recovery}}=31.2^\circ\text{C}$, $T_{\text{final}}=31.5^\circ\text{C}$, insert is the enlargement memory effect curve; (b) molecular glass (Data from Kovacs [4], figure from Zheng and McKenna [12]).