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# Isochoric structural recovery in molecular glasses and its analog in colloidal glasses

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## **Isochoric structural recovery in molecular glasses and its analogue in colloidal glasses**

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### **Abstract**

Concentrated colloidal dispersions have been regarded as models for molecular glasses. One of the many ways to compare the behavior in these two different systems is by comparing the structural recovery or the physical aging behavior. However, recent investigations from our group to examine structural recovery in thermosensitive colloidal dispersions have shown contrasting results between the colloidal and the molecular glasses. The differences in the behaviors of the two systems have led us to pose the question, “Is structural recovery behavior in colloidal glasses truly distinct from that of molecular glasses or is the conventional experimental condition (Isobaric temperature jumps) in determining the structural recovery in molecular glasses different from the experimental condition in the colloidal experiments (Concentration/volume-fraction jumps); i.e., are colloidal glasses inherently different from molecular glasses or not?” To address the question, we resort to new model calculations of structural recovery in a molecular glass under constant volume (Isochoric) conditions following only temperature and simultaneous volume and temperature jumps, which are closer to the volume fraction-jump conditions used in the thermosensitive-colloidal experiments. The current model predictions are then compared with the signatures of structural recovery under the conventional isobaric state in a molecular glass and with structural recovery behavior in colloidal glasses following volume fraction-jumps. We show that the results obtained from the experiments conducted by our group were contrasting to classical molecular glass behavior because the basis of our comparisons were incorrect (the histories were not analogous). The present calculations (with analogous histories) are qualitatively closer to the colloidal behavior. The signatures of ‘intrinsic isotherms’ and ‘asymmetry of approach’ in the current isochoric model predictions are quite different from those in the classical isobaric conditions while the ‘memory’ signatures remain essentially the same. While there are qualitative similarities between the current isochoric model predictions and results from colloidal glasses, it appears from the calculations that the origins of these are different. The isochoric histories in the molecular glasses have compensating effects of pressure and departure from equilibrium which determines the structure dependence on mobility of the molecules. On the other hand, in the colloids it simply appears that the volume fraction jump conditions simply do not exhibit such structure mobility dependence. The determining interplay of thermodynamic phase variables in colloidal and molecular systems might be very different or at least their correlations are yet to be

ascertained. This topic requires further investigation to bring the similarities and differences between molecular and colloidal glass-formers into fuller clarity.

**Keywords:** Colloidal Glasses, molecular glasses, Isochoric, Isobaric, TNM-KAHR model, structural recovery, structural relaxation, physical aging, enthalpy relaxation.

## 1. Introduction

Colloidal dispersions are often considered as models for molecular systems as they display many similar dynamics and due to their ease in visualization [1,2]. Of interest, here is that colloidal glasses are touted as models for studying glass transitions in molecular systems [3,4]. Most work in colloidal glasses have focused on the behavior of the dynamics as a function of concentration/volume-fraction; there has also been some interest in their aging behavior after shear melting perturbations of the glassy structure [5-8]. Then, much like molecular glasses which are in a state of nonequilibrium and continuously evolve towards equilibrium, the evolution of the response can be followed as a function of aging time or waiting time after the perturbation [9,10]. The general observation for molecular systems is that the glass transition occurs when molecular mobility with decreasing temperature becomes such that the material properties, such as specific volume or enthalpy, can no longer “keep up” with the cooling rate and the system “falls out” of equilibrium below a certain temperature referred to as the glass transition temperature. The glass-formation in molecular systems is also associated with a rapidly slowing dynamics in equilibrium that shows a so-called super-Arrhenius temperature dependence in the viscosity or the relaxation time [11-13]. However, the glass transition in colloids is inherently different as colloids are athermal with the control parameter being the concentration rather than, e.g., temperature, pressure, or volume. Hence, the colloidal glass transition is generally associated with a rapid slowing of the dynamics as a function of increasing concentration, with the nominal glass transition concentration being approximately 58% for hard spheres [14,15], though this value is sometimes disputed [4,16]. Unlike molecular glasses where it is relatively easy to change temperature to traverse the glass transition temperature, in colloidal glasses changing volume fraction to traverse the glass concentration is somewhat more difficult, with the result that there are fewer methods to interrogate the glassy nature of colloids than for molecular systems.

In molecular systems, after a temperature-jump away from equilibrium (or a metastable equilibrium) the thermodynamic quantities, such as volume and enthalpy, of a glass evolve with time to reach the equilibrium state relevant to the PVT point of interest. This phenomenon is called physical aging and the change in properties is called structural recovery [17,18]. Generally, structural recovery is studied by observing the change in volume or enthalpy with time following a single temperature jump at a constant

pressure. The change is quantified in terms of the departure from equilibrium or the fictive temperature [19,20]. The two can be related [20] and here we deal with the departure from equilibrium. The departure from equilibrium,  $\delta$  of any measurable thermodynamic quantity, e.g., enthalpy, can be defined as  $\delta_H(t) = [\Delta H(t) - \Delta H(\infty)]$  [21].  $\Delta H(t)$  is the change in enthalpy along the glass line and  $\Delta H(\infty)$  is the change in enthalpy along the extrapolated equilibrium/ liquid line. A similar procedure can be used to determine the volume departure from equilibrium,  $\delta_V = \frac{V(t) - V(\infty)}{V(\infty)}$  [21]. The quantity, departure from equilibrium,  $\delta$  (of the concerned thermodynamic property, in this case either volume or enthalpy) evolves with time to reach zero (equilibrium). Structural recovery is inspected by plotting the evolution of departure from equilibrium,  $\delta$  with time,  $t$ . The time taken by  $\delta$  to reach equilibrium ( $\delta = 0$ ) is called its equilibration time,  $t_{eq}$ .

For molecular systems, Kovacs [22] catalogued three sets of experiments to determine the evolution of a glassy sample during structural recovery. The signatures of these three experiments for a molecular glass are shown in Figure 1 (a) - (f). The first experiment is the ‘Intrinsic Isotherm’. In this experiment the sample is quenched rapidly from a temperature at or above the glass transition temperature ( $T_g$ ) to a temperature below the transition temperature and the change in  $\delta$  is recorded with time. This temperature history is shown in Figure 1(a). The response to the history is given by plotting the departure from equilibrium,  $\delta$  with time,  $t$  as shown in the Figure 1(b). As seen in Figure 1(b) molecular glasses show a very large change in equilibration time as the temperature of the test decreases, consistent with the super-Arrhenius dependence of dynamics [23]. Importantly, this equilibration time follows closely the so-called  $\alpha$ -relaxation time of the system, though some decoupling of the two times have been reported [12,24-32].

The second experiment in the Kovacs catalogue is the ‘Asymmetry of Approach’. In this experiment the departure from equilibrium for the down-jump is compared with the departure from equilibrium for an up-jump; the magnitudes of the up-and down-jumps being the same, Figure 1(c). The down-jump is the same as one of the intrinsic isotherm curves. In the up-jump a sample in equilibrium is heated rapidly to the higher temperature; the final temperature being the same for the up- and down-jumps. The evolution of the departure from equilibrium for the two jumps are compared. Molecular glasses under isobaric conditions show significant asymmetry in the up and down jumps as shown in Figure 1(d). This test shows that the dependence of molecular mobility on its structure during structural recovery is nonlinear in nature.

The third experiment in the catalogue is the ‘Memory’ experiment. In this two-step process the sample is first quenched from the liquid state above  $T_g$  to a glassy state. The sample is then allowed to recover partially with time followed by a temperature up-jump to a new temperature, which Kovacs chose so that

the initial departure from equilibrium after the up-jump step would be near to zero given by Figure 1(e). The experiment is repeated for different magnitudes of the quench and partial recovery times and compared. Figure 1(f) shows the crossover peak response associated with this two-step temperature history for a molecular glass. The peak magnitudes and positions are found to be dependent on the magnitude of the first down jump and the partial aging time. The memory test provides an evidence that the relaxation is nonexponential in nature and that it is path-dependent.

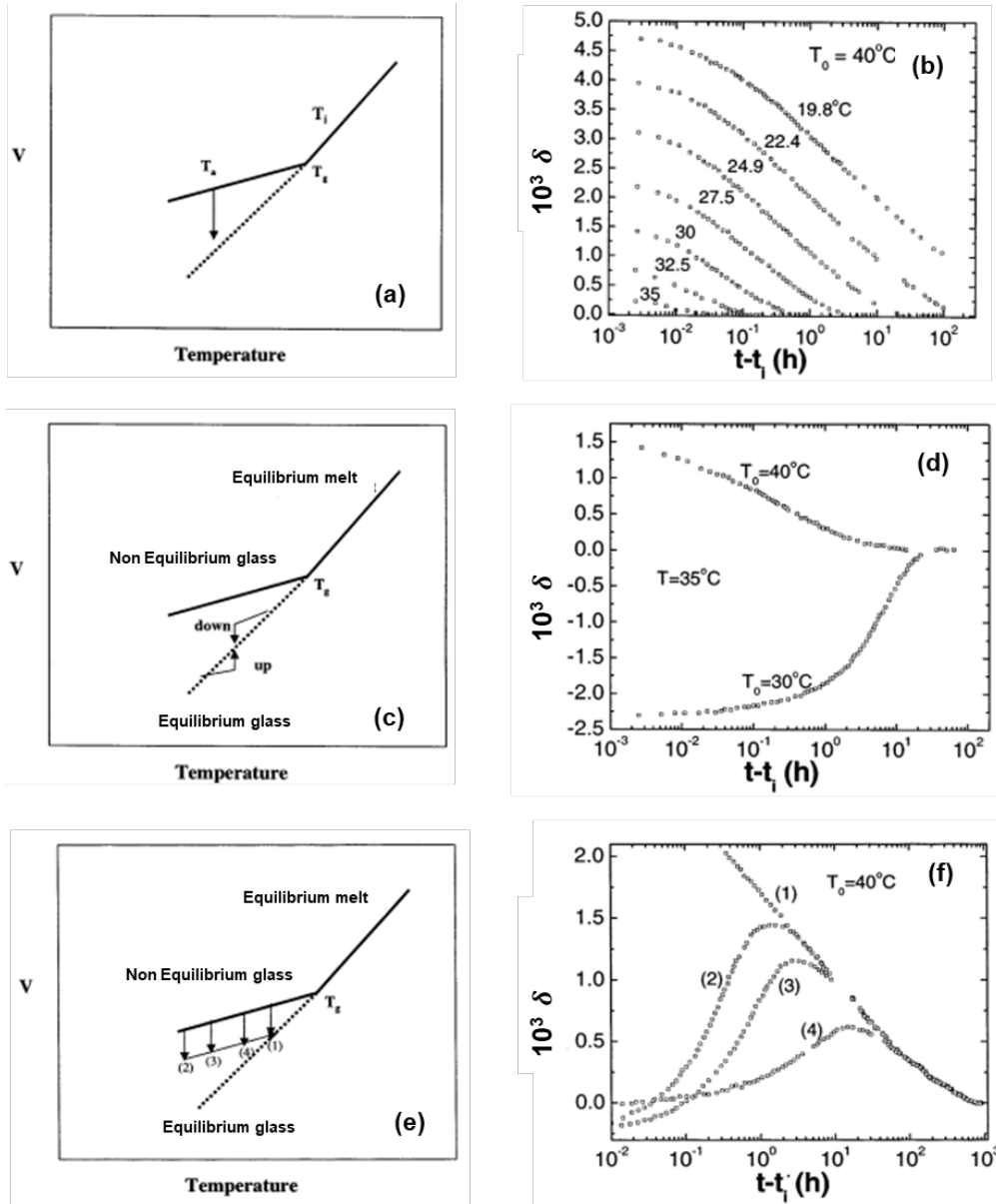


FIG 1. Kovacs three experiments for molecular glasses, plot of volume departure from equilibrium,  $\delta_V$  with aging time,  $t$

*(a) Intrinsic Isotherm-History (b) Intrinsic Isotherm- Signature (c) Asymmetry of Approach- History (d) Asymmetry of Approach- Signature (e) Memory- History (f) Memory- Signature*

*Figures reprinted with permission from Zheng, Y. and G.B. McKenna, Structural recovery in a model epoxy: Comparison of responses after temperature and relative humidity jumps. *Macromolecules*, 2003. **36**(7): p. 2387-2396,[33]. Copyright (2003) by the American Chemical Society.*

To compare the structural recovery behavior in colloidal glasses, the above-mentioned Kovacs' experiments [22,34] for colloidal systems were investigated by McKenna and coworkers [24-26,35]. In case of colloidal systems, the glass transition is traversed by an increase in volume fraction followed by aging at a constant volume fraction. To obtain the Kovacs' type signatures the experiments were conducted using thermosensitive particle dispersions. The diameter of the thermosensitive particles so used increased with decreasing temperature which allows one to change and control the volume fraction with only temperature changes.

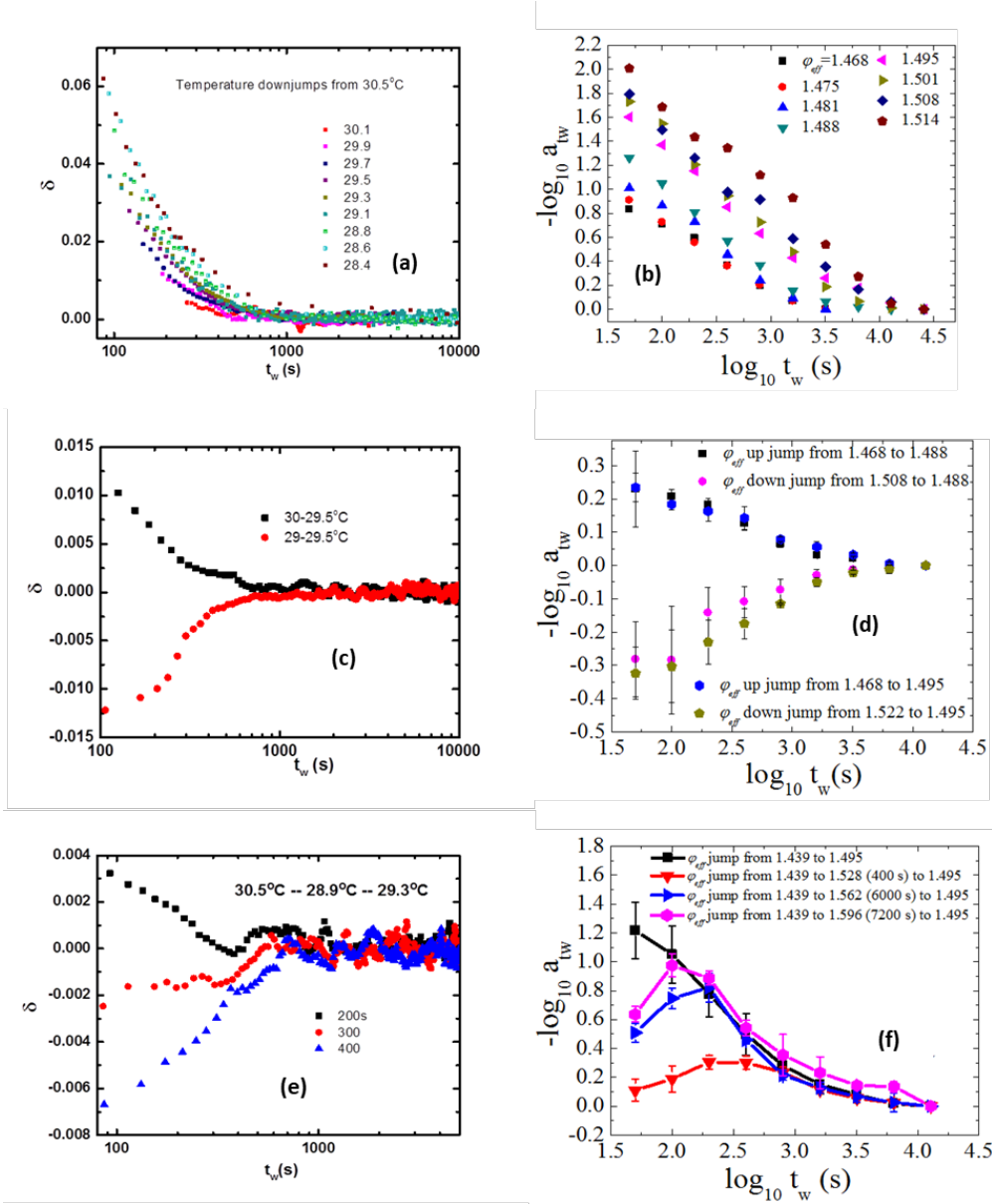


FIG 2. (a), (c) and (e) are the Kovacs' type experiments for thermosensitive colloidal glass measured by Diffusive Wave Spectroscopy, plot of departure from equilibrium,  $\delta$  with aging time,  $t_w$ .

(b), (d) and (f) Kovacs' type experiments for thermosensitive colloidal glass measured by Rheology, plot of shift factors,  $a_{tw}$  with logarithm of aging time,  $t_w$ .

(a) and (b) are the Intrinsic Isotherms; (c) and (d) are Asymmetry of Approach; (e) and (f) are the Memory signatures.

Figures (a), (c) and (e) are reprinted with permission from Di, X.J., X.G. Peng, and G.B. McKenna, Dynamics of a thermo-responsive microgel colloid near to the glass transition. *Journal of Chemical Physics*, 2014. **140**(5).[24]. Copyright (2014) by AIP).

Figures (b), (d) and (f) are reprinted with permission from Peng, X.G. and G.B. McKenna, Physical aging and structural recovery in a colloidal glass subjected to volume-fraction jump conditions. *Physical Review E*, 2016. **93**(4) [35]. Copyright (2016) by the American Physical Society).

In the ‘Intrinsic Isotherm’ experiment, the colloidal glass transition is traversed following a volume fraction jump induced by the temperature jump. So, intrinsic iso-volume fraction is a more fitting description than intrinsic isotherm for this experiment. Figures 2 (a) and (b) show the structural recovery response in the intrinsic volume fraction experiments measured by DWS and rheology respectively. The intrinsic iso-volume fraction curves for the colloids show equilibrium times that are relatively insensitive to the final volume fraction at which the structural recovery or aging takes place. Perhaps more importantly, these equilibration times are significantly different from the structural  $\alpha$ -relaxation times and have a different concentration dependence as shown in Figures 3 (a) and (b). From the figures, it is observed that time to equilibrate,  $t_{eq}$  does not diverge with volume fraction as the  $\alpha$ -relaxation times ( $\tau_\alpha$ ) do. This result is different from what is observed for molecular systems in which both  $t_{eq}$  and  $\tau_\alpha$  diverge in a super-Arrhenius manner [17,18]. Figure 3 clearly shows a decoupling between the equilibration times and the relaxation times in the colloidal dispersions, the reasons for which are still unknown.

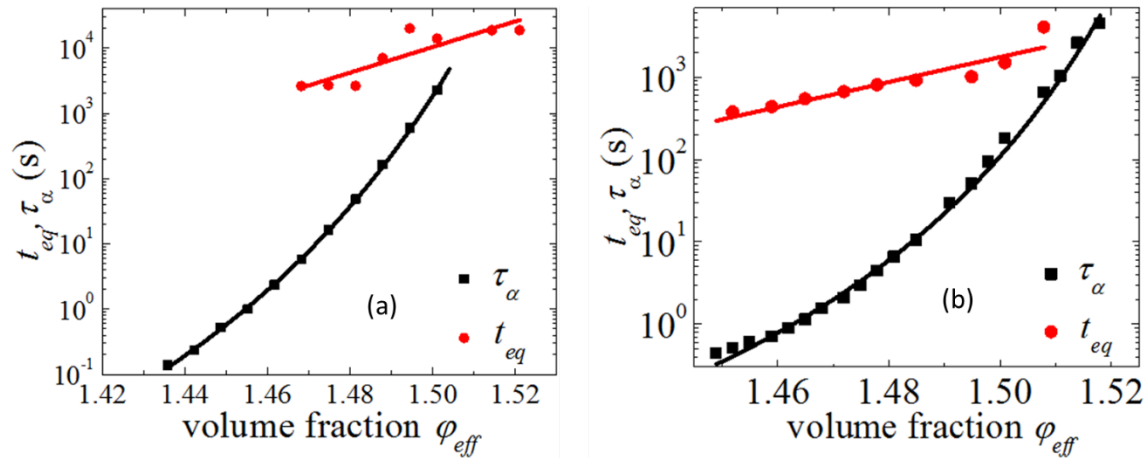


FIG 3. Example of the decoupling between the  $\alpha$ -relaxation time ( $\tau_\alpha$ ) and the time to equilibrate ( $t_{eq}$ ) in the intrinsic iso-volume fraction experiment for a soft colloidal system, as observed from (a) rheological experiment (b) for DWS experiments.

Figure reprinted with permission from X. Peng and G.B. McKenna, “Physical aging and structural recovery in a colloidal glass subjected to volume-fraction jump conditions,” *Phys. Rev. E.*, **93**, 042603 (2016) [35]. Copyright (2016) by the American Physical Society.

The ‘Asymmetry of Approach’ experiment in colloids was performed by comparing the response to an equal up and down jump in volume fraction induced by temperature. The Asymmetry in colloidal glasses is found to be perceptibly less than in molecular glasses as observed in Figures 2 (c) and (d).

The memory results from colloidal glasses are more perplexing. Diffusing wave spectroscopy (DWS) results (Figure 2 (e)) showed no observable memory peak whereas results from rheology measurements (Figure 2 (f)) showed memory.



The signatures of classical Kovacs' experiments on molecular glasses (Figure 1) and Kovacs type experiments on colloidal glasses (Figure 2) along with Figure 3 shows significant differences. These differences in results open the question as to whether structural recovery behavior in colloidal and molecular glasses are similar or not. However, we would like to remark that the histories of the test to inspect structural recovery in these two systems are different; temperature jumps followed by aging in isobaric condition in molecular glasses compared to concentration jumps followed by aging in iso-concentration condition in colloidal glasses. In the current work, we investigate whether the aging conditions (iso-concentration/iso-volume fraction) in the colloids are the same as the aging conditions (isobaric) used by Kovacs for molecular glasses, viz., might isochoric structural recovery in molecular glasses be a more appropriate comparison to make with the colloidal behaviors.

Prior work by Simon and coworkers [36] while investigating structural recovery in nanopores reported results that suggested an accelerated aging similar to the colloidal behavior. The data were well described with a isochoric phenomenological model. To make comparisons with the iso-volume fraction type of experiment in colloids we build on the model put forward by Simon et.al [36] and model the Kovacs' experiments in isochoric aging conditions following a volume and temperature jump. This is described next.

## 2. Isochoric Structural Recovery Modeling

In the colloidal aging experiments, rheological measurements were conducted following volume fraction jumps. These experiments were performed on temperature-sensitive particles i.e. the size of the colloidal particles was temperature controlled. The volume fraction jumps were induced by a temperature step; analogous to a temperature quench in a molecular glass. Also, in a colloidal system, a given volume fraction resembles a unique state of volume in a molecular glass; a volume fraction jump would then correspond to jumps from one volume state to another. Since the size of the colloidal particles was temperature controlled, a jump in volume fraction would be analogous to a simultaneous volume and temperature jump in a molecular glass. Hence, a  $\phi(T)$  jump in a thermosensitive colloidal glass would correspond to a simultaneous  $V, T$  jump in a molecular glass. Once the new volume fraction is reached, the sample ages in the iso-volume fraction condition. Hence it is reasonable to assume that aging in colloids happens in isochoric-like conditions. It is also possible, in a molecular glass, to perform aging experiments at constant volume conditions with only changing temperature, i.e. in isochoric conditions. We also consider this condition here. For the sake of simplicity, we refer to classical isobaric temperature-jump experiments as being in 'Isobaric condition', temperature-jumps experiments at constant volume as

an ‘Isochoric T-jump condition’, and the simultaneous volume and temperature jumps at constant volume as ‘Isochoric VT-jump condition’.

Figure 4 explains the path for the isochoric VT-jump condition. In the figure, the variables that evolve with time (pressure, enthalpy) are plotted against temperature. The material is initially at equilibrium near its glass transition temperature at the state A. The temperature and volume of this state of the material are  $T_0$  and  $V_0$ , respectively. At some time, the temperature and volume are changed from  $T_0V_0$  to  $T_1V_1$  (state B) as shown by the path AB. The path AB depends on how the volume of the system is changed with temperature. In an actual experiment the volume- and temperature-jump would take place at a fast but a finite rate. However, we have modeled the temperature- and volume-jumps at an infinitely fast rate for ease of calculation. Aging begins once the desired volume and temperature is reached. The sample upon aging reaches its new equilibrium line (state C) corresponding to the new volume state,  $V_1$ .

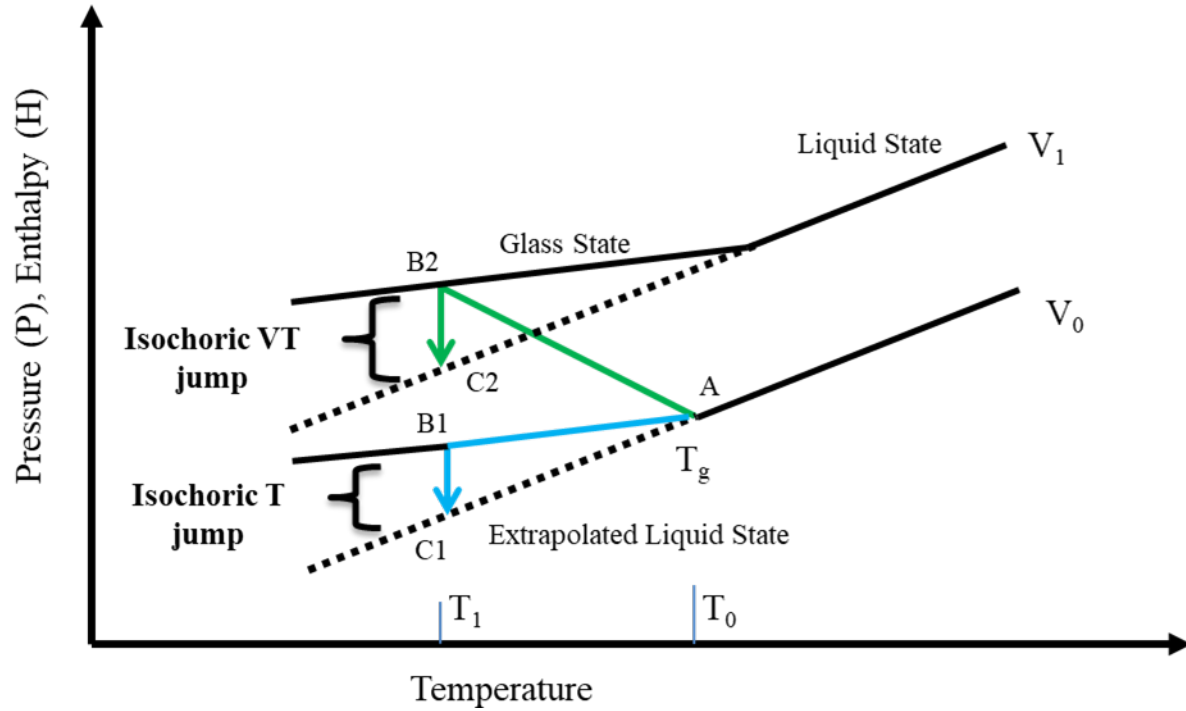


FIG 4. Pressure or Enthalpy vs Temperature for the constant volume (isochoric) condition. Figure shows the liquid and the glass lines at two different volumes (isochores),  $V_0$  and  $V_1$ . The dotted lines show the extrapolated liquid lines for the two isochores. The path AB2 is the path for the simultaneous temperature and volume jump (Isochoric VT-Jump) condition from  $T_0V_0$  to  $T_1V_1$ . The path AB1 is for temperature jump only (Isochoric T-Jump) condition from  $T_0V_0$  to  $T_1V_0$ .

Here, the Kovacs' type experiments are modeled but in constant volume (isochoric) conditions during aging. As the volume remains constant during aging the viscoelastic pressure response is assumed to change in the same manner as the enthalpy. We compare aging signatures in Isochoric T-jump and Isochoric V-jump conditions with the Isobaric conditions. The current isochoric predictions are also compared with the structural recovery responses observed in the colloidal glasses. In the next section, we

develop the model and give the governing equations. It is also worth remarking here that, to our knowledge, the isochoric Kovacs signatures have not been previously examined for molecular glasses either by experiment or modeling.

## 2.1 Model Development

The Tool- Narayanaswamy- Moynihan (TNM) [19,37,38] and Kovacs-Alcoutlabi-Hutchinson-Ramos (KAHR) [20,39,40] model is used to predict the responses to the Kovacs-type structural recovery histories. The TNM-KAHR model is well established in predicting responses of molecular glasses following isobaric temperature jump histories [19-21,34,36,41,42]. Narayanaswamy [37] and Moynihan et.al [19] in their seminal works had first developed a model to predict the inherent nonlinear and nonexponential behavior of structural recovery in inorganic glasses. In their formulation, they have a relaxation time as a function of both temperature and fictive temperature with an Arrhenius temperature dependence. A stretched exponential or the KWW (Kohlrausch-Williams-Watts) [43,44] relaxation function was used to describe structural relaxation. Moynihan in his work showed model calculations with excellent agreement to data to several phenomena observed during aging in inorganic glasses including enthalpy relaxation, memory crossover, enthalpy overshoot and so on. Kovacs [20] in his formulation developed a similar model but used a structure shift factor parameter instead of the fictive temperature to explain the nonlinearity in the system. The relaxation function used was a sum of exponentials. He also showed that the two formulations were interchangeable. The calculations were in excellent agreement to his three signature experiments performed on polymeric glasses. Prior work by Simon et.al [21,36] has combined the two models by using the structure shift factor and a stretched exponential in the relaxation function to describe the structural recovery behavior in both polymeric and molecular glasses.

In the model, the activation energy is assumed to be constant, hence the material has an Arrhenius type temperature dependence. The assumption is valid over small temperature ranges. Therefore, the model works equally for strong and fragile glass formers over the typically small temperature perturbations used in experiment. Simon et.al [1] and Moynihan et.al [2] have used this model to predict enthalpic departure for both fragile and strong glass formers respectively. For different glass formers (fragile or strong) the parameter that would change in the analysis is the apparent activation energy,  $\Delta h^*$ , in addition to the material properties like  $\Delta\alpha$  or  $\Delta C_p$ .

The model includes parameters to explain the nonlinear and the nonexponential behavior of the structural recovery and utilizes reduced time in linearizing the problem. A KWW function is used to describe the recovery behavior. The nonequilibrium behavior is quantified by  $\delta$ . The subscript 'H' in  $\delta_H$

is used for enthalpy. In the isochoric T-jumps the enthalpy changes and evolves following a change in temperature and in the isochoric VT-jumps, the enthalpy changes and evolves in response to the step-changes in both temperature and volume.

Since we are calculating the departure of enthalpy from equilibrium, we need to derive the change in equilibrium enthalpy as a function of the state parameters. To calculate the change in enthalpy in the equilibrium state with change in volume and temperature we use partial derivatives of the thermodynamic properties and the Maxwell's identities [45].

$$H = H(V, T) \quad (1)$$

$$dH = \frac{\partial H}{\partial T} dT + \frac{\partial H}{\partial V} dV \quad (2)$$

$$dH = C_v dT + P dV + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV \quad (3)$$

$$dH = C_v dT + [T(\alpha K)] dV \quad (4)$$

$C_v$  is the heat capacity at constant volume,  $\alpha$  is the volume expansion coefficient and  $K$  is the bulk modulus.  $\alpha_l$ ,  $\alpha_g$  are the volumetric expansion coefficient of the liquid and the glassy states, respectively.  $K_l$ ,  $K_g$  are the bulk modulus of the liquid and the glassy states, respectively. The initial departure from equilibrium,  $\delta_{H_0}$  for the isochoric VT-jump condition is calculated by estimating the difference between the enthalpies in the liquid and the glassy states. The change in pressure with volume and temperature for the isochoric state can be written in terms of the partial derivatives.

$$P = P(V, T) \quad (5)$$

$$dP = \frac{\partial P}{\partial T} dT + \frac{\partial P}{\partial V} dV \quad (6)$$

$$dP = (\alpha K) dT - \left( \frac{K}{V} \right) dV \quad (7)$$

Taking  $dV = 0$  in equation 7 we get the change in pressure for the isochoric T-jump condition. For isobaric aging, the pressure is constant. The thermodynamic properties along the glass and liquid PVT surfaces are obtained and extrapolated from literature data [46,47].

The TNM-KAHR model estimates the departure from equilibrium,  $\delta$  as

$$\delta_H = \delta_{H_0} \exp \left[ - \left( \int_0^t \frac{dt}{\tau} \right)^\beta \right] \quad (8)$$

The expression inside the brackets is the KWW function.  $\beta$  is the nonexponential parameter in the KWW function. For a volume jump condition the departure from equilibrium is calculated at each isochore by calculating the difference in enthalpies in the present state of the glass and the corresponding state of equilibrium. For a simultaneous volume and temperature jump from  $T_0, V_0, P_0$  to  $T_1, V_1, P_1$ ,

$$\delta_{H_0} = (C_{v_l} - C_{v_g})(T_0 - T_1) \quad (9)$$

An appropriate change in pressure is calculated in the model per the change in volume during the volume jump. As the material is viscoelastic, the pressure is time dependent and is given by Boltzmann superposition principle [48]

$$P = P_{ref} + \alpha_g K_g (T_1 - T_0) - \frac{K_g}{V_1} (V_1 - V_0) + \left[ (\alpha_l K_l - \alpha_g K_g) (T_1 - T_0) - \frac{K_g}{V_1} (V_1 - V_0) \right] \left\{ 1 - \exp \left[ - \left( \int_0^t \frac{dt}{\tau} \right)^\beta \right] \right\} \quad (10)$$

$T_{ref}, P_{ref}$  are the temperature and pressure at the reference state.  $P_{ref}$  is taken as the ambient pressure of 1 bar.  $T_{ref} = T_0$  is the glass transition temperature ( $T_g$ ) as determined by DSC.

The relaxation time and the shift factors are given by equations 11 - 14. [36,39,40,49,50]

$$\tau = \tau_{ref} a_T a_P a_\delta \quad (11)$$

$$a_T = e^{-\theta_T (T - T_{ref})} \quad (12)$$

$$a_\delta = e^{-\theta_\delta \delta} \quad (13)$$

$$a_P = e^{\theta_P (P - P_{ref})} \quad (14)$$

$$\theta_T = \Delta h^* / R T_g^2 \quad (15)$$

$$\theta_\delta = (1 - x) \theta_T / \Delta C_p \quad (16)$$

$\tau_{ref}$  is the relaxation time at the reference temperature.  $a_T$ ,  $a_P$  and  $a_\delta$  are the temperature, pressure and structure shift factors, respectively.  $\theta_T, \theta_P, \theta_\delta$  are material constants in the shift factors.  $\theta_T$  and  $\theta_\delta$  are given by equations 15 and 16 [39,40].  $\Delta h^*$  is the apparent activation energy.  $x$  is the nonlinearity parameter that partitions the relative effects of  $T$  or  $P$  and  $\delta$ .  $R$  is the universal gas constant. The

numerical values of  $\beta, \chi, \Delta h^*, \theta_T, \theta_P$  and  $\theta_\delta$  are taken from [36] in which  $\theta_P$  was used as a fitting parameter. The values of the parameters for ortho-terphenyl (oTP) are given in the Table I.

Equations 8, 9 and 10 were solved with the help of MATLAB R2016b to obtain the evolution of departure from equilibrium,  $\delta_H$  with time,  $t$ . The equilibration time,  $t_{eq}$  is determined as the time taken by  $\delta_H$  to reach  $10^{-3}$  J/g.

Table I. Parameters used in the model calculations. The parameters are for ortho terphenyl (oTP)[36]

Parameter	Value
$\Delta C_p \text{ (cal g}^{-1}\text{K}^{-1}\text{)}$	0.13
$C_{p_l} \text{ (cal g}^{-1}\text{K}^{-1}\text{)}$	0.342
$\alpha_l \text{ (10}^{-4}\text{K}^{-1}\text{)}$	7.34
$\alpha_g \text{ (10}^{-4}\text{K}^{-1}\text{)}$	2.57
$K_l \text{ (GPa)}$	2.56
$K_g \text{ (GPa)}$	3.70
$V_g \text{ (cm}^3\text{g}^{-1}\text{)}$	0.893
$\theta_T \text{ (K}^{-1}\text{)}$	0.63
$\theta_P \text{ (bar}^{-1}\text{)}$	0.020
$\theta_\delta$	2.67
$\ln \tau_{ref} / s$	5.5
$\beta$	0.7
$\Delta H \left( \frac{kcal}{mol} \right)$	75
$\chi$	0.45
$T_g, T_{ref} \text{ (K)}$	242.1
$P_{ref} \text{ (bar)}$	1

## Results

The intrinsic isotherm calculated from the TNM-KAHR model is given in Figure 5 for the isobaric (a), isochoric T-jump (b) and isochoric VT-jump (c) and (d) conditions. The different isotherms in each figure are for different jump magnitudes in temperature and volume. It is evident from the Figure 5 (a)

that a higher magnitude of jump throws the system farther from equilibrium. Higher departure from equilibrium in Figure 5 (a-isobaric) than 5 (b-isochoric) for the same steps in temperature is due to a higher magnitude of  $C_P$  than  $C_V$ . In figures, (c) and (d) the departures from equilibrium are higher than (b) due to the contributions from both temperature and volume. A comparison of Figures 5 (c) and (d) with (b) shows that large departures from equilibrium can be achieved by either temperature or volume jump or both. In Figure 5 (a), the time to reach equilibrium,  $t_{eq}$  increases exponentially with the increase in magnitude of the jump in the isobaric case. The equilibration times in the isobaric condition changes by 4 orders of magnitude for a change in jump magnitude from 1°C to 15°C. However, this trend weakens in the isochoric conditions. The changes in equilibration times reduce to less than three orders of magnitude in the case of the purely isochoric T-jump condition and less than one order of magnitude for the isochoric VT-jump condition, Figures 5 (b) and (c), (d) respectively. To better understand the contributions of the volume and temperature we did the volume jump simulations in two different ways. First, we modeled the departure from equilibrium for a constant volume jump but for different temperature jumps as shown in Figure 5 (c) and second for different volume jumps but constant temperature jump, as shown in Figure 5 (d). However, a reduced sensitivity of the equilibration times relative to the isobaric condition (Figure 5a) is observed when the temperature jump is constant as shown in Figure 5 (d). Comparing Figures 5 (c) and (d), the equilibration times increased by more than two orders of magnitude when the temperature jump was varied. However, the change in equilibration times increased by less than an order of magnitude when the volume jump was varied. The possible origins of this behavior are examined subsequently in the discussion section.

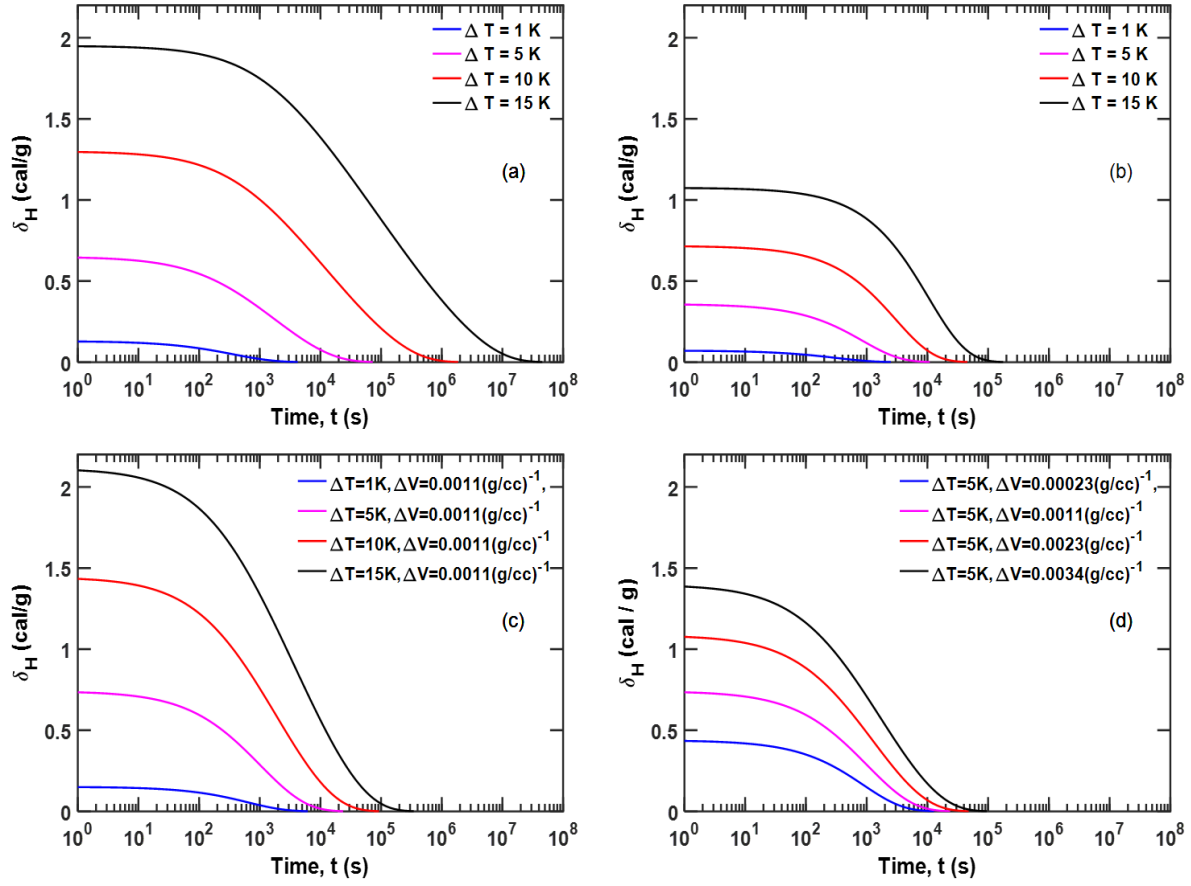


FIG 5. Departure from equilibrium for (a) isobaric T-jump (b) isochoric T-jump (c) isochoric VT-jump conditions with constant volume jumps (d) isochoric VT-jump conditions with constant temperature jumps

The asymmetry of approach observed in molecular glasses are thought to be due to the dependence of the relaxation kinetics on the instantaneous structure of the system, i.e. due to the structure shift factor  $a_\delta$  at least in the case of isobaric experiments. Hence, in the down-jump condition the response is more rapid than the up-jump condition because the approach to equilibrium in the former case takes place in the condition of excess volume relative to equilibrium, while in the latter case, the response is slowed by the reduced molecular mobility related to a deficit of volume. The results from the TNM-KAHR model calculations for the asymmetry of approach for the isobaric, isochoric T-jump and isochoric VT-jump conditions are given in Figures 6 (a), (b) and (c) respectively. The asymmetry is clearly visible in the isobaric condition shown in Figure 6 (a) and is more pronounced than in either of the isochoric histories in Figures 6 (b) and (c). It is observed that a constant volume constraint during aging diminishes the asymmetry between the up and down jumps. The asymmetry in the isochoric VT-jump condition is more than the isochoric T-jump condition. In the case of the VT-jump condition, the equilibration times,  $t_{eq}$  for



the up and down jumps are slightly different. Deviations between the up and down jump equilibration times increase upon increasing the jump magnitudes and the asymmetry in the VT-jump curves become more prominent. The purely isochoric T jumps don't show any significant change in symmetry even at large jump magnitudes. Since the asymmetry is a result of the structural difference in the state at the beginning of the test, a diminished asymmetry suggests that constant volume during aging plays an important role in determining the relaxation kinetics.

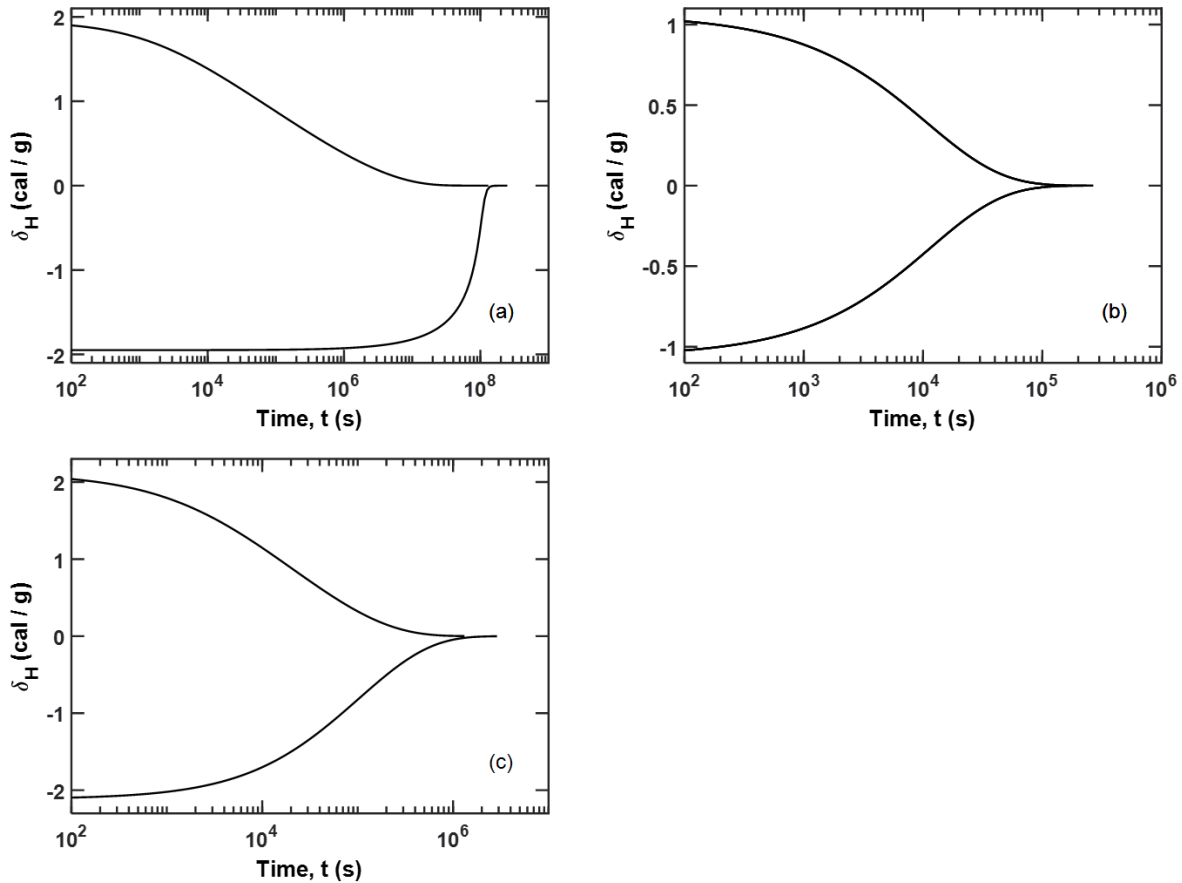


FIG 6. Asymmetry of approach for a jump magnitude of  $15^{\circ}\text{C}$  (a) Isobaric T-jump (b) Isochoric T-jump (c) Isochoric VT-jump. A large jump magnitude of  $15^{\circ}\text{C}$  is chosen to magnify the difference between (b) and (c).

The memory effect is the consequence of the Boltzmann superposition of the nonexponential response of the system to its history [49]. Each of the isobaric, isochoric T-jump and VT-jump conditions show similar memory as seen in Figures 7 (a), (b) and (c). Peak position and magnitude depend on the jump magnitude in all three conditions and no perceptible difference in the trends is found. A comprehensive comparison can't be readily made with the colloidal glasses. The colloidal systems do not have a clear departure from equilibrium of a thermodynamic state-like variable such as  $\delta_H$  or  $\delta_V$ .

Furthermore, diffusing wave spectroscopy (DWS) results showed little or no significant memory, while the rheological experiments showed a typical memory response as measured by the shift factors describing the time-waiting time superposition of the creep responses after the relevant concentration jumps, as depicted in Figures 2 (e) and (f) [35]. The difference in dynamics observed by macro rheological and micro rheological (DWS) techniques suggest the inability of the latter method to capture some essential physics during aging. It is of interest to establish what the light scattering technique measures in the microscopic dynamics for a system out of equilibrium as compared to the macrorheological measurements.

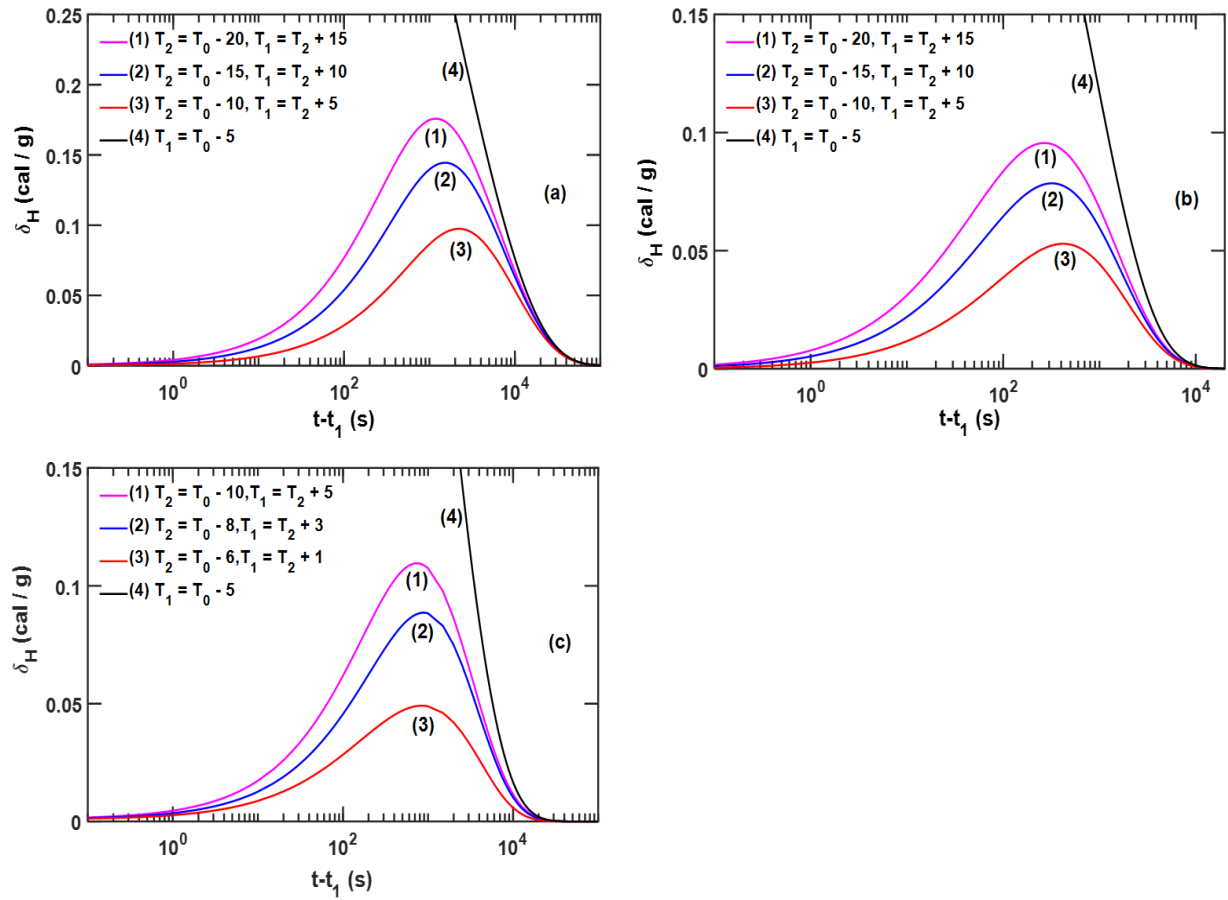


FIG 7. Memory signatures for (a) Isobaric T-jump (b) Isochoric T-jump (c) Isochoric VT-jump. In each figure, curves (1), (2) and (3) are the two step histories with different magnitudes of jumps. (4) is the direct quench to the same final temperature/volume.

The partial equilibration times are: (a) Isobaric: (3)- 8244 s, (2)- 15193 s, (1)- 37696 s; (b) Isochoric: (3)- 1805 s, (2)- 2942 s, (1)- 6321 s; (c) Isochoric VT-Jump: (3)- 919 s, (2)- 7075 s, (1)- 24881 s.

The magnitudes of temperature jumps are given in the plots. For figure (c), the volume jumps for the different lines are: (4)-  $0.0011 \text{ (g/cc)}^{-1}$ , (3)-  $0.0014$  and  $-2.3 \times 10^{-4} \text{ (g/cc)}^{-1}$ , (2)-  $0.0018$  and  $-6.8 \times 10^{-4} \text{ (g/cc)}^{-1}$ , (1)-  $0.0023$  and  $-0.0011 \text{ (g/cc)}^{-1}$ .

## Discussion

In the previous section, we have presented the behavior for the structural recovery response of a small molecule glass-forming liquid in isobaric and isochoric conditions when subjected to temperature and volume jumps and compared with the results from experiments on thermosensitive colloidal systems. The findings shown above suggest that the direct comparison of the isobaric Kovacs signatures in molecular systems with those for iso-volume fraction experiments in colloids may not be the correct comparison to make. The impetus is to compare the present isochoric model results with the observed results from iso-volume fraction jump experiments on thermosensitive colloidal systems that have shown significant differences from the isobaric responses. At the same time, the similarities with the isochoric conditions need further exploration because the possible origins of the similarities may be only fortuitous. Here we describe and discuss what we observed.

### *Intrinsic Isovolume-fraction Jumps vs. Intrinsic Isotherms*

Figures 2 (a) – (f) show that the colloidal systems display a significantly weaker dependence on time, for the system to equilibrate for jumps increasingly deep into the glassy state than what is seen in the molecular glass. Upon carrying out the TNM-KAHR model calculations for the intrinsic isotherm in either isochoric VT-jump or isochoric T-jump conditions, we see that the spreading of the times to equilibrate is much weaker than in the isobaric conditions. This is seen in Figures 5 (a) through (d). Figure 5 shows that large departures from equilibrium can be achieved by either temperature or volume jump or both. However, the equilibration times don't spread for Figure 5 (d) when the temperature jump is maintained constant at a low magnitude. It is unclear how the colloid and the molecular glass compare in this case. In a molecular glass, there is a pressure and an enthalpy departure from equilibrium that are needed to fully describe the response. Whether the same structural parameters play an equivalent role for the iso-volume fraction colloid as it evolves towards equilibrium is less clear. Also, in molecular glass the jump is in temperature and volume from one state to another while in colloidal glass it is a jump in volume fraction alone. However, qualitative similarity of Figure 5 (d) with colloidal iso-volume fraction jump responses emphasizes on the importance of absence of temperature in determining relaxation kinetics in colloidal glasses.

### *Asymmetry of Approach*

As indicated previously, in the isobaric experiments the asymmetry occurs because the molecular mobility depends on both temperature and structure, the latter through the departure from equilibrium of the glass, here defined in terms of the enthalpic departure from equilibrium. During a temperature down

jump the sample starts at a high enthalpy and the enthalpy recovers with time to its equilibrium value in a way that Kovacs considered as auto retarded. In the temperature up-jump case, the mobility is reduced because of the low initial enthalpy and the system evolves in an auto accelerated way as the molecular mobility increases with increasing enthalpy during the evolution towards equilibrium. This dependence of molecular mobility on the structure of the system causes the asymmetry in the molecular systems. The colloids on the other hand show no or very little asymmetry (Figures 2 (c), and (d)). In the case of the isochoric calculations the asymmetry is very weak, similar to the weak asymmetry observed in colloidal experiments. But examining the terms that lead to the asymmetry in the isochoric case gives some insight into the origins for the molecular glass model. In the isochoric case, the pressure shift factor  $a_P$  and the structure shift factor  $a_\delta$  both play a role in the molecular mobility during the evolution of the structure towards equilibrium. It turns out that the  $a_P$  and the  $a_\delta$  term act in opposite directions to compensate the tendency towards an asymmetry. Hence the isochoric glass appears to be much less asymmetric than does the isobaric glass. In case of the colloidal system interplay of different parameters like pressure and departure from equilibrium to determine the structural recovery response is not yet known. In fact, symmetrical behavior in asymmetry of approach response suggests that the colloidal glass may not exhibit the nonlinearity normally associated with the molecular glasses. Nonlinearity in terms of a structure dependence of the relaxation time, is given by the TNM-KAHR nonlinearity parameter ' $\chi$ ', ( $0 \leq \chi \leq 1$ ). If this interpretation is correct, it suggests that the colloidal systems are like molecular glasses without a structure dependence of the relaxation time, or  $\chi = 1$ . It may further suggest, as postulated by McKenna, Narita and Lequeux [10,51] that the colloidal response is more related to simple perturbations from equilibrium, similar to stress or strain perturbations in fading memory materials, though perhaps with limits on the analogy due to the discreteness of the colloidal particles.

### Memory Effect

The memory effects seen in the colloidal system by macroscopic rheology are similar to those seen in both the experimental isobaric T-jumps for molecular glasses and for the calculations for isobaric and isochoric jumps from the TNM-KAHR model. The idea that this response is dominated by the Boltzmann superposition of the thermal, volume histories seems consistent with this response. Hence, it is clear that the colloidal systems do show memory in the classic sense for the sorts of histories considered. Quantitative modeling would appear to be a next step in understanding these responses.

For the present study, it is important to keep in mind that for a molecular system, the interplay of the thermodynamic state-like parameters is crucial and determines the relaxation kinetics. Within the TNM-KAHR framework, the dynamics of a molecular system are explained based on the thermodynamic variables like pressure, volume, temperature or entropy. For a Brownian system like a colloid, the

relevance of these thermodynamic variables is not well understood. Correlating the similarities and differences between the two different systems is complicated as the controlling parameters are different. The current work implies the apparent differences in structural relaxation behavior in colloids and molecular systems are influenced by the conditions in which the experiments are conducted. Absence of temperature and a dependence of the dynamics on only volume fraction is suggested to be crucial in the aging behavior of a colloidal system. Observation of the insensitivity of equilibration times with jump magnitude and symmetrical up and down jumps when a constant volume is maintained during aging in our calculations using the TNM-KAHR model argue in favor of our interpretations of the model. From the model calculations, a higher asymmetry in the isobaric responses than the isochoric responses suggest a greater sensitivity of the molecular mobility to the glassy structure. On the other hand, in the isochoric conditions, the structure and the pressure shift factors were found to compensate each other which leads to a weakening of the asymmetry. This seems responsible for symmetric up and down jump responses in the isochoric TNM-KAHR system. Whether this same analogue for the colloids can be made or not remains an open question as a compelling analogue of the structure shift factor in the colloids is yet to be ascertained., viz., how the structure of the colloidal system influences the relaxation time during structural recovery is yet to be determined. This makes it unclear whether the same counterbalancing mechanism would play a role in determining the structural recovery behavior in the colloidal dispersion.

Finally, the weak or lack of a memory effect in measurements by DWS raises questions on the limitations and the applicability of the measuring technique itself. While the nonequilibrium state of the colloid can be argued to explain a lack of agreement between the DWS and the macroscopic rheology, it remains an important question as to what can be learned from the DWS experiments.

### 3. Conclusions

Model predictions of the Kovacs's type experiments on molecular glasses in isochoric conditions using the TNM-KAHR framework are presented in this work. Multiple important results were obtained. The structural recovery response of a molecular glass in isochoric histories were found to be different than the classical Kovacs' findings in isobaric conditions. Based on the similarities and differences in model predictions and experimental results it appears that the observed structural recovery behavior in colloidal glasses under volume fraction jump conditions is closer to the aging in a molecular glass under isochoric volume jump condition.

The isochoric histories showed very weak asymmetry of approach behavior. This result is similar to those observed for colloidal systems subjected to volume fraction jump conditions. Comparison of the present model predictions with experiments on colloidal system establishes that constant volume fraction

during aging plays a role in determining the Kovacs' type signatures in colloids. Because the colloidal systems have more limited structure parameters that can influence the dynamics, the origins of the similarities and differences between the constant volume fraction system and the isochoric molecular glass seem to be different. For example, in the asymmetry of approach experiment the molecular glass calculations using the TNM-KAHR model suggest that there are competing effects of pressure and enthalpy departure from equilibrium on the molecular mobility. The result is very little asymmetry, unlike the isobaric case where the enthalpy departure (or volume departure) vary during the experiment and pressure (and temperature) are constant. In the case of the colloids we postulate that there is an insignificant nonlinearity of the response and that the lack of asymmetry is simply due to this feature of colloidal behavior, viz., it is essentially linear in the range of responses seen in volume-fraction jump conditions and the nonlinearity parameter  $\chi$  of the TNM-KAHR model would be equal to unity. There is no structure dependence of the molecular mobility in colloidal glasses. In the isochoric intrinsic isotherm histories, the VT-jump condition showed equilibration times weakly sensitive to the jump magnitude. This result is closer to intrinsic iso-volume fraction curves in colloidal systems and contrary to the super-exponential increase in times for isobaric conditions. The resemblance between the colloidal results with isochoric VT-jump condition and its differences with the isobaric condition suggests that the differing dynamics in colloidal and molecular glasses is influenced by the constant volume constraint in both the systems and the temperature or rather by the absence of it in the colloids. Similar memory effects were observed for the isochoric and isobaric aging conditions, consistent with the macrorheological responses observed for the colloidal volume fraction experiments. Finally, we assert that the differences in dynamics of the nonequilibrium system seen by DWS and classical rheological experiments demand further investigation. The question to ask is “what does one learn from the DWS on nonequilibrium systems that augments our understanding of dynamics?” Acknowledging the drawbacks of DWS will help us to develop newer methods in studying physics of condensed matter and in better understanding of nonequilibrium systems.

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