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

Sourya Banik and Gregory B. McKenna[*]
Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409-3121, USA

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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 this 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- or volume fraction-jumps); i.e., are colloidal glasses inherently different from molecular glasses or not? To address the question, we resort to model calculations of structural recovery in a molecular glass under constant volume (isochoric) conditions following temperature only- 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.

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I. 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 has focused on the behavior of the dynamics as a function of concentration or 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.

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[*] Corresponding author: greg.mckenna@ttu.edu

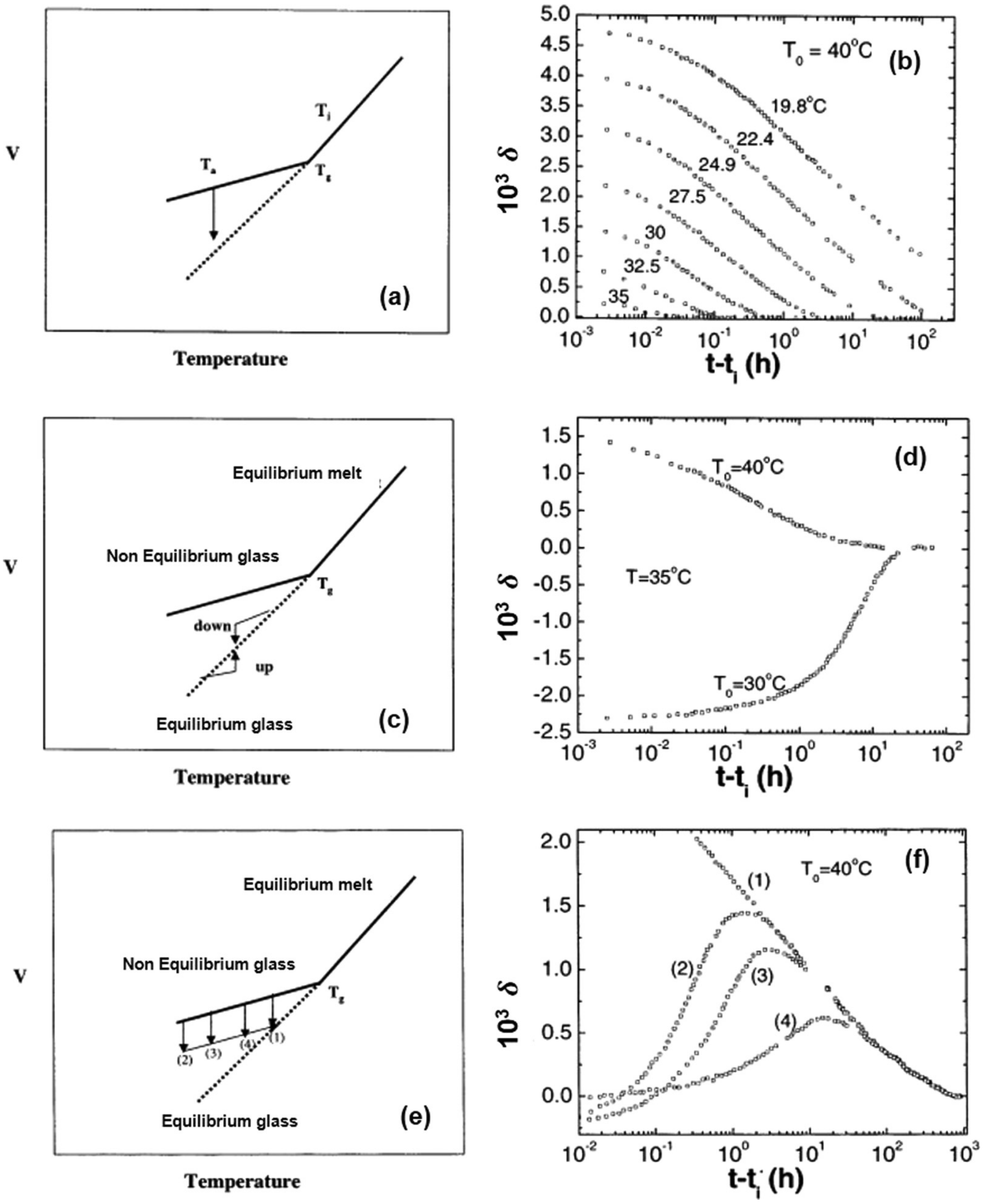

FIG. 1. Kovacs three experiments for molecular glasses, plot of volume departure from equilibrium δ_V with aging time t. (a) Intrinsic isotherm: history. (b) Intrinsic isotherm: signature. (c) Asymmetry of approach: history. (d) Asymmetry of approach: signature. (e) Memory: history. (f) Memory: signature. Figure reprinted with permission from Zheng and McKenna [33]. Copyright 2003 by the American Chemical Society.

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 pressure, volume, temperature (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 δ 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 or 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 δ (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 δ with time t. The time taken by δ to reach equilibrium ($\delta = 0$) is called its equilibration time t_{eq}.

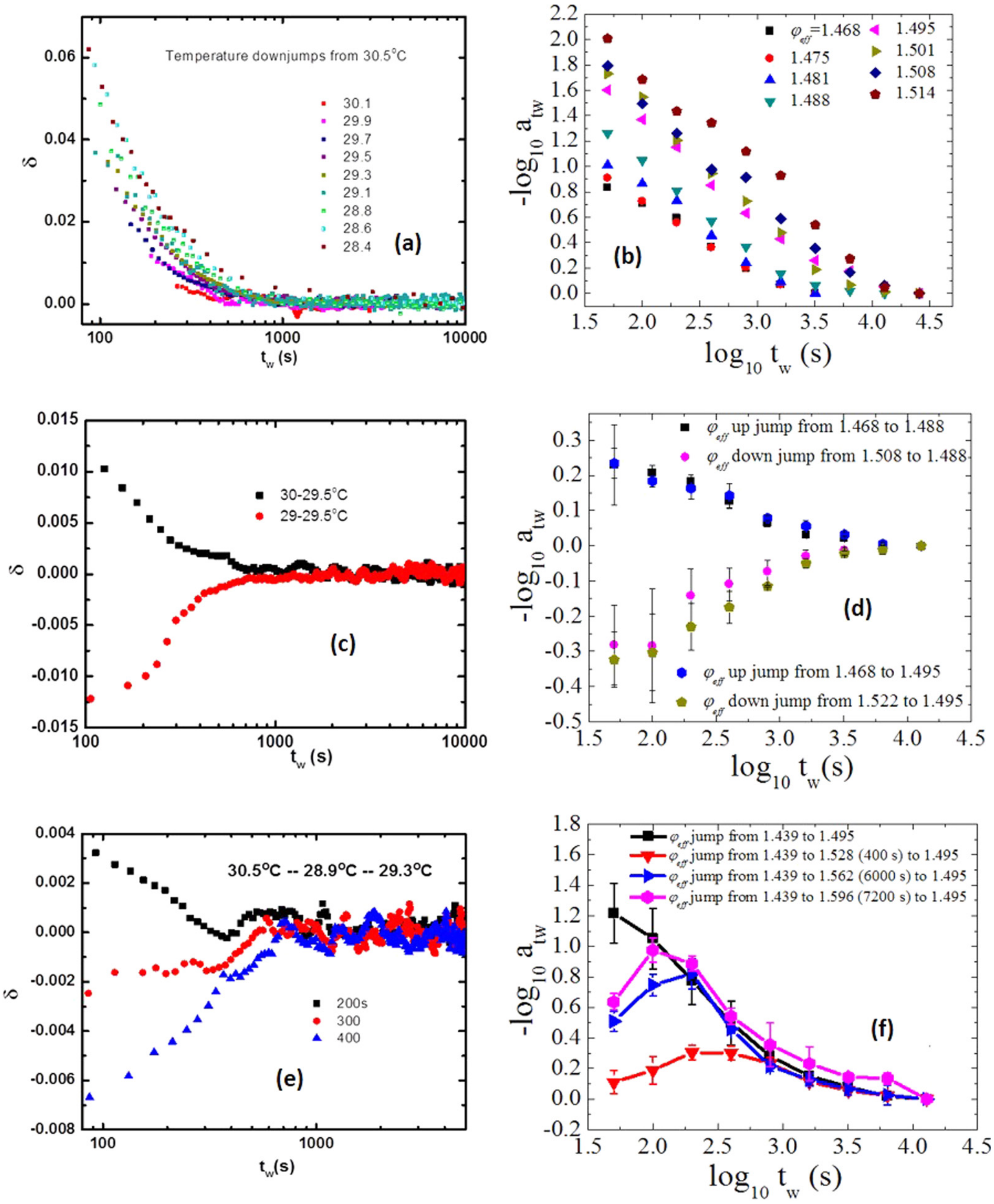

FIG. 2. (a), (c), and (e) are the Kovacs type experiments for thermosensitive colloidal glass measured by diffusive wave spectroscopy; plot of departure from equilibrium δ with aging time t_W. (b), (d), and (f) Kovacs type experiments for thermosensitive colloidal glass measured by rheology, plot of shift factors a_{tw} with logarithm of aging time t_W. (a), (b) Intrinsic isotherms. (c), (d) Asymmetry of approach. (e), (f) Memory signatures. Panels (a), (c), and (e) are reprinted with permission from Di, Peng, and McKenna [24]. Copyright 2014 by AIP. Panels (b), (d), and (f) are reprinted with permission from Peng and McKenna [35]. Copyright 2016 by the American Physical Society.

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 Figs. 1(a)–1(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 δ is recorded with time. This temperature history is shown in Fig. 1(a). The response to the history is given by plotting the departure from equilibrium δ with time t as shown in Fig. 1(b). As seen in Fig. 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 α-relaxation time of the system, though some decoupling of the two times has been reported [12,24–32].

The second experiment in the Kovacs catalog 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, Fig. 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 is compared. Molecular glasses under isobaric conditions show significant asymmetry in the up- and down-jumps as shown in Fig. 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 catalog 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 zero given by Fig. 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 evidence that the relaxation is nonexponential in nature and that it is path dependent.

To compare the structural recovery behavior in colloidal glasses, the above-mentioned Kovacs' experiments [22,34] for colloidal systems were investigated by McKenna and co-workers [24–26,35]. In the 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.

In the intrinsic isotherm experiment, the colloidal glass transition is traversed following a volume fraction-jump induced by the temperature-jump. So, intrinsic isovolume fraction is a more fitting description than intrinsic isotherm for this experiment. Figures 2(a) and 2(b) show the structural recovery response in the intrinsic volume fraction experiments measured by DWS and rheology respectively. The intrinsic isovolume 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 α-relaxation times and have a different concentration dependence as shown in Figs. 3(a) and 3(b). From the figures, it is observed that time to equilibrate, t_{eq}, does not diverge with volume fraction as the α-relaxation times (τ_α) do. This result is different from what is observed for molecular systems in which both t_{eq} and τ_α 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.

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 Figs. 2(c) and 2(d).

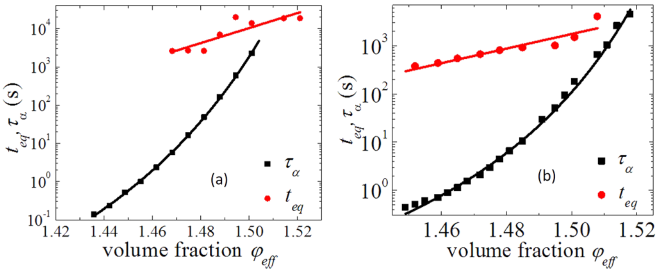

FIG. 3. Example of the decoupling between the α-relaxation time (τ_α) and the time to equilibrate (t_{eq}) in the intrinsic isovolume fraction experiment for a soft colloidal system, as observed from (a) rheological experiment, (b) DWS experiments. Figure reprinted with permission from Peng and McKenna [35]. Copyright 2016 by the American Physical Society.

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

The signatures of classical Kovacs' experiments on molecular glasses (Fig. 1) and Kovacs type experiments on colloidal glasses (Fig. 2) along with Fig. 3 shows significant differences. These differences in results open the question as to whether structural recovery behavior in colloidal and molecular glasses is 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 conditions in molecular glasses compared to concentration-jumps followed by aging in isoconcentration conditions in colloidal glasses. In the current work, we investigate whether the aging conditions (isoconcentration or isovolume 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 co-workers [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 an isochoric phenomenological model. To make comparisons with the isovolume 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.

II. 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

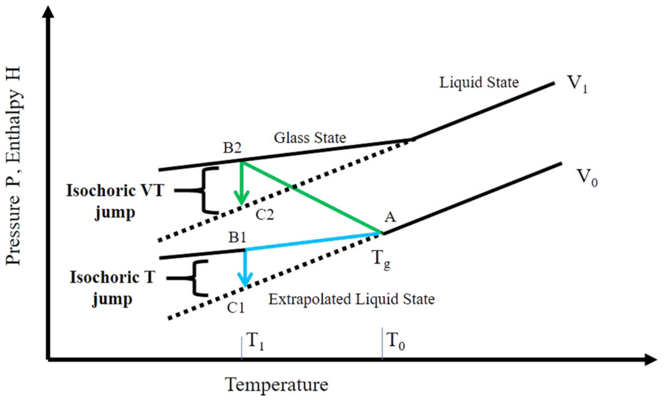

FIG. 4. Pressure or enthalpy vs temperature for the constant volume (isochoric) condition. Figure shows the liquid and the glass lines at two different volumes (isochores), V_0 and V_1. The dotted lines show the extrapolated liquid lines for the two isochores. The path AB2 is the path for the simultaneous temperature and volume-jump (isochoric *VT*-jump) condition from $T_0 V_0$ to $T_1 V_1$. The path $AB1$ is for temperature-jump only (isochoric *T*-jump) condition from $T_0 V_0$ to $T_1 V_0$.

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 isovolume fraction condition. Hence it is reasonable to assume that aging in colloids happens in isochoriclike 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-jump 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 $T_0 V_0$ to $T_1 V_1$ (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 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.

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.

A. 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 Δh^*, in addition to the material properties like $\Delta\alpha$ or ΔC_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 δ. The subscript "*H*" in δ_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 identities [45],

$$H = H(V,T), \tag{1}$$

$$dH = \frac{\partial H}{\partial T} dT + \frac{\partial H}{\partial V} dV, \tag{2}$$

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

$$dH = C_v dT + [T(\alpha K)] dV. \tag{4}$$

C_v is the heat capacity at constant volume, α is the volume expansion coefficient, and K is the bulk modulus. α_l, α_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 δ_{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,

$$P = P(V,T), \tag{5}$$

$$dP = \frac{\partial P}{\partial T} dT + \frac{\partial P}{\partial V} dV, \tag{6}$$

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

Taking $dV = 0$ in Eq. (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 δ as

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

The expression inside the brackets is the KWW function. β 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,

$$\delta_{H_0} = (C_{vl} - C_{vg})(T_0 - T_1). \tag{9}$$

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]

$$\begin{aligned} P = {} & P_{\text{ref}} + \alpha_g K_g (T_1 - T_0) - \frac{K_g}{V_1}(V_1 - V_0) \\ & + \left[(\alpha_l K_l - \alpha_g K_g)(T_1 - T_0) - \frac{K_g}{V_1}(V_1 - V_0) \right] \\ & \times \left\{ 1 - \exp\left[-\left(\int_0^t \frac{dt}{\tau} \right)^{\beta} \right] \right\}. \end{aligned} \tag{10}$$

TABLE I. Parameters used in the model calculations. The parameters are for orthoterphenyl (oTP) [36].

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

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

The relaxation time and the shift factors are given by Eqs. (11)–(14) [36,39,40,49,50]:

$$\tau = \tau_{\text{ref}} a_T a_P a_\delta, \tag{11}$$

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

$$a_\delta = e^{-\theta_\delta \delta}, \tag{13}$$

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

$$\theta_T = \Delta h^* / R T_g^2, \tag{15}$$

$$\theta_\delta = (1 - x)\theta_T / \Delta C_p. \tag{16}$$

τ_{ref} is the relaxation time at the reference temperature. a_T, a_P, and a_δ are the temperature, pressure, and structure shift factors, respectively. θ_T, θ_P, θ_δ are material constants in the shift factors. θ_T and θ_δ are given by Eqs. (15) and (16) [39,40]. Δh^* is the apparent activation energy. x is the nonlinearity parameter that partitions the relative effects of T or P and δ. R is the universal gas constant. The numerical values of β, x, Δh^*, θ_T, θ_P, and θ_δ are taken from [36] in which θ_P was used as a fitting parameter. The values of the parameters for orthoterphenyl (oTP) are given in Table I.

Equations (8)–(10) were solved with the help of MATLAB R2016b to obtain the evolution of departure from equilibrium δ_H with time t. The equilibration time t_{eq} is determined as the time taken by δ_H to reach 10^{-3} J/g.

III. RESULTS

The intrinsic isotherm calculated from the TNM-KAHR model is given in Fig. 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 Fig. 5(a) that

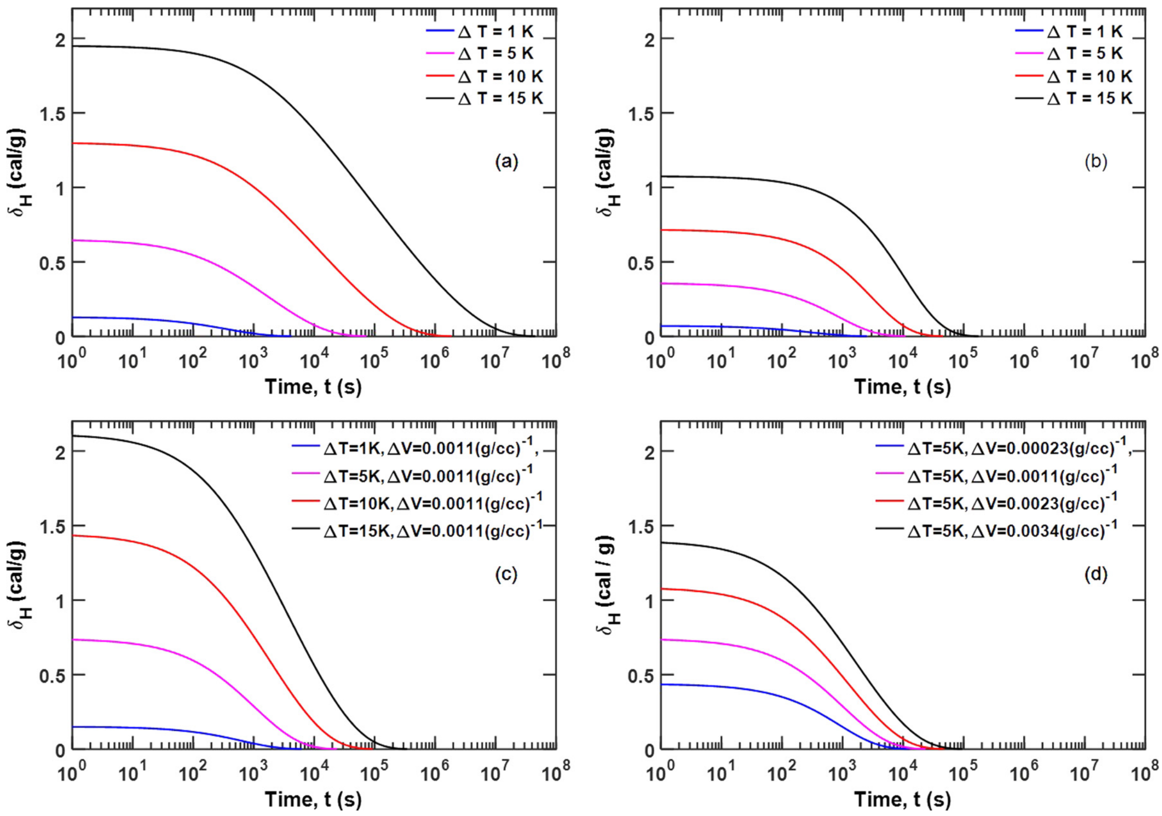

FIG. 5. Departure from equilibrium for (a) isobaric *T*-jump, (b) isochoric *T*-jump, (c) isochoric *VT*-jump conditions with constant volume-jumps, (d) isochoric *VT*-jump conditions with constant temperature-jumps.

a higher magnitude of jump throws the system farther from equilibrium. A higher departure from equilibrium in Fig. 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 Figs. 5(c) and 5(d) the departures from equilibrium are higher than in 5(b) due to the contributions from both temperature and volume. A comparison of Figs. 5(c) and 5(d) with 5(d) shows that large departures from equilibrium can be achieved by either temperature- or volume-jump or both. In Fig. 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 four orders of magnitude for a change in jump in magnitude from 1–15 °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, Figs. 5(b) and 5(c) and 5(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 Fig. 5(c) and second for different volume-jumps but constant temperature-jump, as shown in Fig. 5(d). However, a reduced sensitivity of the equilibration times relative to the isobaric condition [Fig. 5(a)] is observed when the temperature-jump is constant as shown in Fig. 5(d). Comparing Figs. 5(c) and 5(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.

The asymmetry of approach observed in molecular glasses is 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_δ 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 Figs. 6(a)–6(c) respectively. The asymmetry is clearly visible in the isobaric condition shown in Fig. 6(a) and is more pronounced than in either of the isochoric histories in Figs. 6(b) and 6(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 do not show any significant change in symmetry even at large jump

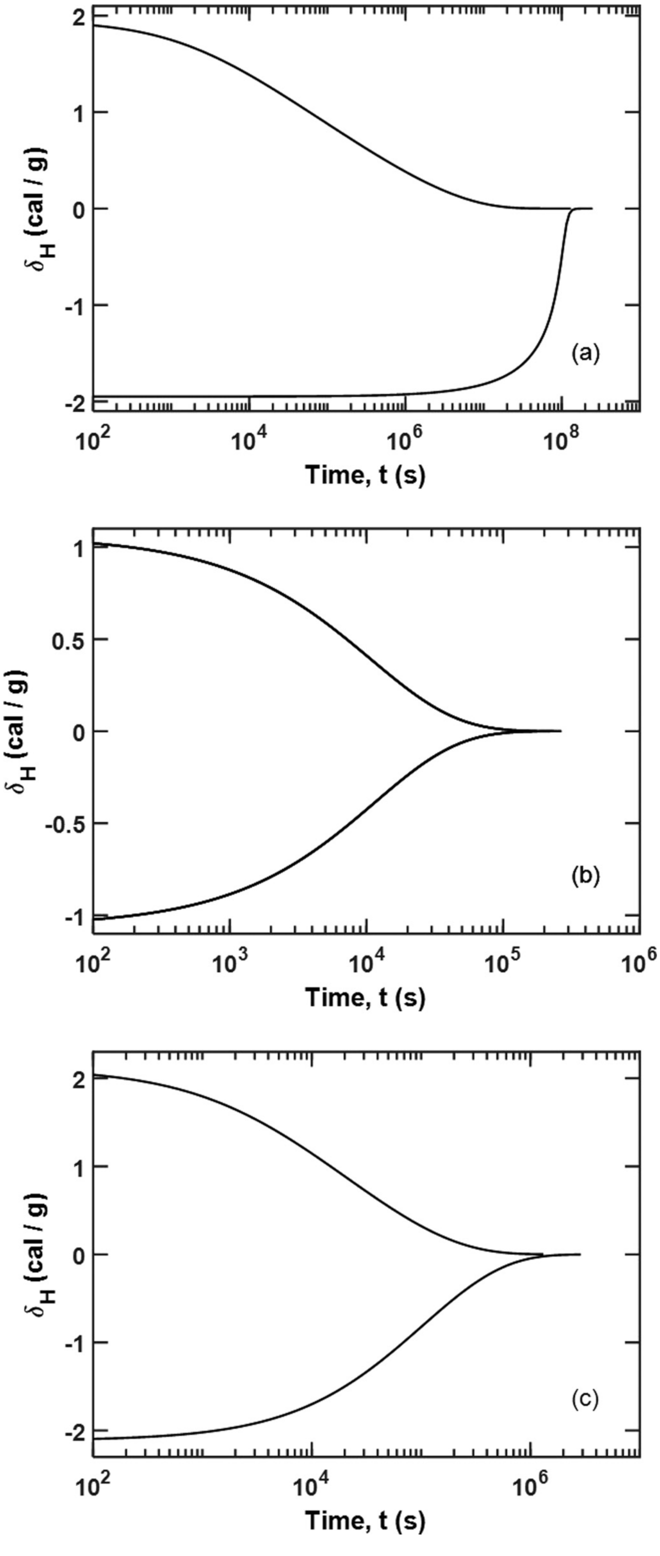

FIG. 6. Asymmetry of approach for a jump magnitude of 15 °C (a) isobaric *T*-jump, (b) isochoric *T*-jump, (c) isochoric *VT*-jump. A large jump magnitude of 15 °C is chosen to magnify the difference between (b) and (c).

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.

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 shows similar memory as seen in Figs. 7(a)–7(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 cannot be readily made with the colloidal glasses. The colloidal systems do not have a clear departure from equilibrium of a thermodynamic statelike variable such as δ_H or δ_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 Figs. 2(e) and 2(f) [35]. The difference in dynamics observed by macrorheological and microrheological (DWS) techniques suggests 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.

IV. 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 isovolume 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 isovolume 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.

A. Intrinsic isovolume fraction-jumps vs intrinsic isotherms

Figures 2(a)–2(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 Figs. 5(a)–5(d). Figure 5 shows that large departures from equilibrium can be achieved by either temperature- or volume-jump or both. However, the equilibration times do not spread for Fig. 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

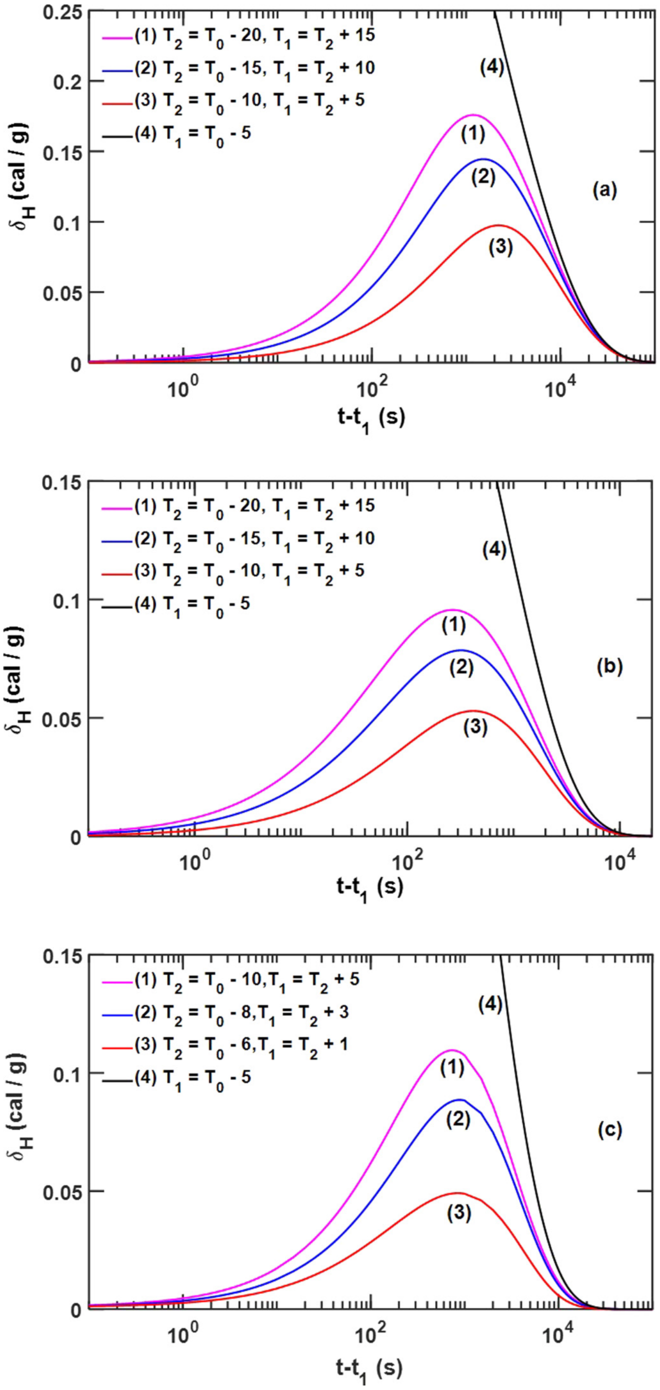

FIG. 7. Memory signatures for (a) isobaric *T*-jump, (b) isochoric *T*-jump, (c) isochoric *VT*-jump. In each panel, curves (1)–(3) are the two step histories with different magnitudes of jumps; (4) is the direct quench to the same final temperature or volume. The partial equilibration times are (a) 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 panel (c), the volume-jumps for the different lines are (4) $0.0011\,(\mathrm{g/cc})^{-1}$, (3) 0.0014 and $-2.3 \times 10^{-4}(\mathrm{g/cc})^{-1}$, (2) 0.0018 and $-6.8 \times 10^{-4}(\mathrm{g/cc})^{-1}$, (1) 0.0023 and $-0.0011(\mathrm{g/cc})^{-1}$.

structural parameters play an equivalent role for the isovolume 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, the qualitative similarity of Fig. 5(d) with colloidal isovolume fraction-jump responses emphasizes on the importance of absence of temperature in determining relaxation kinetics in colloidal glasses.

B. 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 autoretarded. In the temperature up-jump case, the mobility is reduced because of the low initial enthalpy and the system evolves in an autoaccelerated 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 [Figs. 2(c), and 2(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_δ 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_δ 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 the 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 'x' ($0 \leqslant x \leqslant 1$). If this interpretation is correct, it suggests that the colloidal systems are like molecular glasses without a structure dependence of the relaxation time, or $x = 1$. 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.

C. 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 statelike 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 in 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 or not this same analog for the colloids can be made remains an open question as a compelling analog 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 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.

V. CONCLUSIONS

Model predictions of the Kovacs 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 was 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 x 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 isovolume fraction curves in colloidal systems and contrary to the superexponential 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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