# Memory in aging colloidal gels with timevarying attraction

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# Memory in aging colloidal gels with time-varying attraction



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# ABSTRACT

We report a combined rheology, x-ray photon correlation spectroscopy, and modeling study of gel formation and aging in suspensions of nanocolloidal spheres with volume fractions of 0.20 and 0.43 and with a short-range attraction whose strength is tuned by changing temperature. Following a quench from high temperature, where the colloids are essentially hard spheres, to a temperature below the gel point, the suspensions form gels that undergo aging characterized by a steadily increasing elastic shear modulus and slowing, increasingly constrained microscopic dynamics. The aging proceeds at a faster rate for stronger attraction strength. When the attraction strength is suddenly lowered during aging, the gel properties evolve non-monotonically in a manner resembling the Kovacs effect in glasses, in which the modulus decreases and the microscopic dynamics become less constrained for a period before more conventional aging resumes. Eventually, the properties of the gel following the decrease in attraction strength converge to those of a gel that has undergone aging at the lower attraction strength throughout. The time scale of this convergence increases as a power law with the age at which the attraction strength is decreased and decreases exponentially with the magnitude of the change in attraction. A model for gel aging in which particles attach and detach from the gel at rates that depend on their contact number reproduces these trends and reveals that the non-monotonic behavior results from the dispersion in the rates that the populations of particles with different contact number adjust to the new attraction strength.

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# I. INTRODUCTION

Colloidal suspensions become unstable to gelation when attractive interactions between the particles become sufficiently strong. This process is the basis for important applications in areas such as ceramics, food technology, and tissue engineering to name a few. Understanding the mechanisms that dictate the formation and properties of colloidal gels remains a key challenge for soft matter physics, and the phenomenon raises fundamental questions about the nature of out-of-equilibrium systems more broadly. Numerous experimental and theoretical investigations over the past few years have provided insights into the gelation process,<sup>1</sup> and they have revealed mechanisms of gelation for several kinds of colloidal suspensions. For a colloid–polymer mixture, where the attraction between colloids can result from depletion, the gel transition coincides with spinodal-type phase separation of the colloids into a colloid-poor phase and a colloid-rich phase that becomes dynamically arrested.<sup>2-4</sup> For a suspension of colloids where the attraction is induced by an interplay of the functionalized particle surfaces and solvent, the gel transition has been associated with a rigidity percolation transition.<sup>5-7</sup> Recent studies have further recognized the importance of the microstructure formed by the particles in the gelation process.<sup>8,9</sup> Clusters and other hierarchical structures have been observed in several colloidal systems during gelation<sup>10-12</sup> and have inspired new theories of the gel transition.<sup>13,14</sup>

Irrespective of the mechanisms that drive the transition, the gel that forms generally displays slow dynamics that leave it in an out-of-equilibrium state. As such, gels share features with other disordered, out-of-equilibrium systems, such as glasses. For instance, gel properties can depend on the manner in which the gel transition is traversed,<sup>15</sup> and gels can undergo aging that bears similarities with aging in glasses.<sup>16,17</sup> A key feature of glasses and other out-of-equilibrium systems, such as spin glasses, is their ability to possess memory, wherein properties of the system encode and display signatures of its thermal or mechanical history.<sup>18</sup> In this paper, we explore how history dependence and memory are manifest in colloidal gels by studying the response of gels to time-varying strengths of attraction during formation and aging.

To conduct these studies, we employ nanocolloidal suspensions that form thermo-reversible gels, which are ideal systems to investigate gelation with time-varying attraction since the strength of the interparticle interaction can be tuned in situ easily. Previous work on nanocolloidal suspensions forming thermo-reversible gels has revealed interesting aspects of the gelation at fixed particle attractions. Specifically, during formation and aging, gels with different fixed strengths of attraction display dynamic scaling, where each gel proceeds through the apparently same series of intermediate states-represented by the same transient microstructure, microscopic dynamics, and elasticity-and the strength of attraction affects only the pace of this evolution.<sup>19,20</sup> This common set of intermediate states suggests that a gel should not have the ability to retain a memory of the strength of attraction under which it was formed if the attraction strength is changed. As we report below, our studies using time-varying attraction reveal that gels can retain transient memories that manifest in behavior resembling the classic Kovacs effect originally observed in aging polymer glasses.<sup>21,22</sup> Furthermore, the manner in which these memories fade provides insights into the processes driving aging of the gels.

Our experiments focus on gel formation and aging at two volume fractions  $\phi$  of particles,  $\phi = 0.20$ , which is in a regime intermediate between the attractive glass transition at large  $\phi$  and fractal gels at low  $\phi$ , and  $\phi$  = 0.43, which is in the regime of concentrated gels near the boundary with attractive glasses.<sup>5,23-25</sup> Employing the latest x-ray detector technology, we conducted x-ray photon correlation spectroscopy (XPCS) experiments to probe the microstructure and microscopic dynamics during gelation and aging and to capture the evolution of these properties after a change in attraction strength. We further performed rheology measurements to characterize the evolution in mechanical properties and provide a macroscopic characterization of the response of the gels to changes in strength of attraction. Section II describes the preparation of the nanocolloidal suspensions and the experimental techniques. Section III summarizes the results of the experiments, and Sec. IV describes a simple model that reproduces some of the key features of the results, guiding our interpretation. Finally, in Sec. V we conclude.

### **II. MATERIALS AND METHODS**

# A. Sample fabrication

The colloids were synthesized using the Stober method of basecatalyzed hydrolysis and condensation of tetraethylorthosilicate,<sup>26</sup> and a seeded growth technique<sup>27</sup> was used to increase the particle size to a radius of 41 nm (10% polydispersity). The particle surfaces were functionalized with 1-octadecanol, and the particles were dispersed in decalin at two volume fractions,  $\phi = 0.20$  and  $\phi = 0.43$ . When the temperature of the suspensions is below the theta temperature of octadecanol in decalin,  $T_{\theta} \approx 33$  C, the colloids experience a short-range interparticle attraction that can be modeled as a square well with a width of  $\sim$ 1 nm and temperature-dependent depth,

$$U = Ak_B(T_\theta - T), \tag{1}$$

where *A* is about 30.<sup>28</sup> Hence, the strength of attraction can be tuned by adjusting the temperature, and for sufficiently strong attraction, the suspensions transform into a gel. The gel temperature, which corresponds to a critical point<sup>29</sup> associated with rigidity percolation,<sup>30</sup> was found to be 12.5 ± 2.9 and 13.6 ± 0.7 C at  $\phi$  = 0.20 and  $\phi$  = 0.43, respectively [see inset to Fig. 1(a)].

# **B.** Rheometry

Measurements of the complex shear modulus,  $G^*(v) = G'(v)$ + iG''(v), were performed in a cone-plate geometry using a stresscontrolled rheometer (Anton-Paar MCR 300) with an integrated Peltier-based temperature control at a frequency v = 1 Hz and strain amplitude of 0.08% that was well within the linear viscoelastic regime. A typical rheometry measurement to investigate gelation under time-varying attraction began with a quench from room temperature to an initial temperature  $T_i$  below the gel temperature. The suspension was held at  $T_i$  for a certain amount of time,  $t_s$ , during which it underwent the gel transition and obtained solid-like behavior. The temperature was then increased to a final temperature  $T_f$ , which was also below the gel temperature, and the suspension was held there. Unless otherwise stated, the ramp rate was 3 C/min during the initial cooling and 1 C/min during the heating. These cooling and heating rates were chosen as they were close to the fastest achievable without significant undershooting on cooling or overshooting on heating. In addition, the initial temperature  $T_i$  was restricted to the range of relatively shallow quenches that kept the system in the region of homogeneous gel formation identified in the state diagram of Suman and Wagner.<sup>3</sup>

At the end of each measurement, the sample was heated back to room temperature and held there for at least 20 min to fully fluidize it and erase the thermal history. To characterize any time lags between the rheometer thermometry and actual sample temperature, we performed rheometry measurements with the same temperature profiles on a silicone oil with a temperature-dependent viscosity. These measurements indicated that the sample reached a stable temperature ~20 s after the thermometer following changes from  $T_i$  to  $T_f$ .

# C. XPCS

X-ray photon correlation spectroscopy measurements were carried out on the suspension with  $\phi = 0.20$  at sector 8ID-I of the Advanced Photon Source. The sample was contained in a custom-designed cell for transmission small angle x-ray scattering and mounted on the beamline in a Peltier-driven temperature control stage (Quantum Northwest). The same protocols to vary temperature and hence strength of interparticle attraction as those in the rheometry measurements were employed in the XPCS measurements. An additional platinum RTD thermometer was placed within the sample cell to read the sample temperature. Diagnostic measurements showed that the sample temperature lagged the control thermometry such that the sample temperature became stable ~350 s after the control temperature following changes from  $T_i$  to  $T_f$ . As discussed below, this longer thermal time constant of the



**FIG. 1.** (a) Storage (squares) and loss (circles) shear modulus at v = 1 Hz of the suspension with  $\phi = 0.20$  as a function of time following a quench to 6.5 C. The arrow at t = 520 s indicates the gel time at which G' and G'' cross. Inset: Inverse of the logarithm of the gel time as a function of inverse temperature. The solid line shows a linear fit to the data. (b) XPCS correlation functions at wave vector q = 0.03 nm<sup>-1</sup> as a function of delay time from measurements at different times on the suspension with  $\phi = 0.20$  quenched to 6.5 C. (c) Scattering intensity as a function of wave vector from the same measurements as in (b).

XPCS thermometry compared with that in the rheometry led us to perform measurements at larger  $t_s$  in the XPCS measurements. The thermometers in the rheometry and XPCS measurements were calibrated against each other, and the temperatures reported for the two can be compared on the same absolute scale. A partially coherent x-ray beam with energy 10.9 keV and size  $150 \times 15 \ \mu m^2$  (V × H) was focused to a 10 × 15  $\mu m^2$  (V × H) spot on the sample, and a high-frame-rate x-ray area detector (Rigaku UHSS-500K) was positioned 8 m after the sample to measure the scattering over the wave-vector range  $0.01 \le q \le 0.30 \ nm^{-1}$ . XPCS measurements were performed repeatedly while the temperature protocol to form a gel and vary its interparticle attraction was performed. In each measurement, the detector took a series of images at  $5 \times 10^4$  fps for  $1 \times 10^5$  frames, and the beam was translated to a new position of the sample between measurements to avoid radiation damage. The microscopic dynamics were characterized by the autocorrelation function of the scattering intensity

$$g_2(q,\tau) = \frac{\langle I(\mathbf{q},t_m)I(\mathbf{q},t_m+\tau)\rangle}{\langle I(\mathbf{q},t_m)\rangle^2},$$
(2)

where  $I(\mathbf{q}, t_m)$  is the intensity at wave vector  $\mathbf{q}$  and measurement time  $t_m$ ,  $\tau$  is the delay time, and the brackets represent averages over measurement time and over pixels in a small region near wave-vector magnitude q.

## **III. RHEOLOGY AND XPCS RESULTS**

# A. Cel formation and aging at fixed attraction strength

We first summarize the gel formation and aging behavior of the nanocolloidal suspensions at fixed attraction strength. These results are consistent with previous characterizations of the thermoreversible gelation in these suspensions.<sup>19,20,29,32</sup> Figure 1(a) shows the storage and loss moduli of the suspension with  $\phi = 0.20$  following a quench to 6.5 C from room temperature [i.e., introduction of an interparticle attraction,  $U = 2.84k_BT$ , through Eq. (1)]. The time is set to zero when the temperature reaches 6.5 C. Immediately after the quench, the suspension is in a liquid state (G' < G''), and the moduli shows negligible change until about t = 300 s. After this latency period, the moduli begin to increase and the gel transition, taken to be when G' and G'' cross, is reached at  $t_g = 520$  s, as indicated by the arrow in Fig. 1(a). After the transition, the suspension is solid-like (G' > G''), and G' continues to increase steadily. Consistent with previous studies,<sup>16,32</sup> this increase persists indefinitely as the gel ages, with G' eventually growing as a weak power-law,  $G' \propto t^{\alpha}$ , with  $\alpha \approx 0.4$  (see Fig. S1 of the supplementary material). The inset to Fig. 1(a) shows the gel time obtained from quenches to different temperatures. The gel time is a strong function of temperature and increases with increasing temperature (weaker attraction) such that  $t_g \sim \exp[C/(T_g - T)]$ , consistent with previous work that characterized the critical behavior of the gel transition in these nanocolloidal suspensions.<sup>29</sup> Extrapolating to  $t_g \rightarrow \infty$  gives  $T_g = 12.5 \pm 2.9$  C.

Figures 1(b) and 1(c) show  $g_2(q, \tau)$  at  $q = 0.03 \text{ nm}^{-1}$  and the scattering intensity I(q), respectively, from an XPCS experiment on the suspension with  $\phi = 0.20$  at room temperature and at different times following a quench to 6.5 C. The roomtemperature correlation function fully decays in a short delay time showing the particles are freely diffusing. Following the quench to 6.5 C, the dynamics begin to slow and eventually  $g_2(q, \tau)$ becomes non-ergodic within the 2 s measurement time window. An intermediate plateau appears at  $\tau \ge 0.01$  s with a plateau value that rises steadily, which indicates an increasing localization of the particles<sup>33,34</sup> that has a close connection to the emergence of elasticity.<sup>34–36</sup> Detailed analysis of the dynamics described by the XPCS is presented in Refs. 20 and 32. At room temperature, I(q) has a peak near q = 0.065 nm<sup>-1</sup> corresponding to the first interparticle structure factor peak of the hard-sphere fluid and a relatively small value in the low q region, indicating the lack of large-scale structure in the fluid. After the quench, the low q region increases with time, and the structure factor peak steadily decreases, together indicating the formation of a gel network with increasingly predominant large-length-scale microstructure. Notably, these changes in microstructure are not observed during gelation at  $\phi = 0.43$ , which is close to the crossover between the gel and attractive glass states.<sup>32</sup>

# B. Gel response to step change in attraction strength *1. Gel melting and re-formation*

We now describe the response of an aging gel to a sudden decrease in attraction strength. Figures 2(a) and 2(b) show the temperature profile and the evolution of G' and G'', respectively, from a measurement in which the suspension with  $\phi = 0.20$  is first quenched to  $T_i = 6.4$  C and then heated to  $T_f = 8.5$  C ( $U_i = 2.85k_BT$  to  $U_f = 2.61k_BT$ ) at t = 310 s. After the quench, G' and G'' remain small and constant for a latency period of about 100 s and then increase rapidly. The suspension goes through the gel transition (G' = G'') at approximately  $t_g = 260$  s. Following the heating to 8.5 C, both moduli display a period in which they decrease with time. As discussed further below, this transient period of decreasing moduli, which has also been observed in other thermo-reversible gel systems,<sup>16</sup> is a general feature of the response to a decrease in the interparticle attraction. In Fig. 2(b), the decrease in G' is so significant that G'drops below G''; that is, the suspension returns to a fluid state. This fluidization occurs despite the temperature remaining below the gel temperature at all times. Later, the moduli again begin to increase, and the suspension again passes through the gel transition at  $t_{\sigma} = 3500 \text{ s.}$ 

Figures 2(c) and 2(d) show  $g_2(q, \tau)$  and I(q), respectively, from an XPCS experiment with the same temperature sequence. Consistent with the rheology, the evolution in the microscopic dynamics and microstructure is non-monotonic. Following the quench to 6.4 C, the dynamics slow dramatically such that by  $t = 310 \text{ s } g_2(q, \tau) \text{ pos-}$ sesses only a small decay to a plateau. Coincident with this slowing, I(q) at low q grows rapidly, signaling the formation of large-scale structure. After the suspension is heated to 8.5 C, the dynamics became significantly faster, as shown by the correlation functions at t = 470 s and t = 600 s, indicating the particles regain fluidlike mobility, and the low q region of I(q) decreases, indicating partial dissolution of the large-scale structure. This reversal of the gel formation lasts ~250 s, after which  $g_2(q, \tau)$  and I(q) show a re-initiation of the gel formation. This transient reversion is seen more clearly in Figs. 3(a) and 3(b), which show the evolution of  $g_2(q, \tau)$  at q = 0.09 nm<sup>-1</sup> and  $\tau = 0.1$  s and I(q)at two wave vectors, respectively. After the quench to 6.4 C,  $g_2(q, \tau = 0.1 \text{ s})$  sharply increases from one as the dynamics slow and the intermediate plateau forms. After the temperature reaches 8.5 C,  $g_2(q, \tau = 0.1 \text{ s})$  decreases back to one before slowly increasing again. Similarly, as seen in Fig. 3(b),  $I(q = 0.03 \text{ nm}^{-1})$  increases rapidly at 6.4 C, indicating the



**FIG. 2.** (a) The temperature and (b) the storage and loss moduli of the suspension with  $\phi = 0.20$  as a function of time from a measurement in which the suspension was quenched to 6.4 C and then heated to 8.5 C after 310 s. The two arrows at 260 and 3500 s indicate the crossover times of G' and G'' at 6.4 and 8.5 C, respectively. The dashed vertical lines in (a) and (b) indicate  $t_s = 310$  s. (c) Correlation functions at wave vector q = 0.09 nm<sup>-1</sup> as a function of delay time at different times from an XPCS measurement with the same thermal history as in (a). (d) Scattering intensities as a function of wave vector at different times from the same measurement as in (c).



**FIG. 3.** (a) XPCS correlation function at  $q = 0.09 \text{ nm}^{-1}$  and  $\tau = 0.1 \text{ s}$  and (b) scattering intensities at q = 0.03 and 0.07 nm<sup>-1</sup> as functions of time from the same measurement as in Figs. 2(c) and 2(d) along with results from a measurement at 8.5 C throughout. The dashed vertical lines indicate  $t_s = 310 \text{ s}$ .

formation of large-scale structure, then shows a large decrease after the attraction is weakened, only to begin increasing again. This dissolution and re-formation of large-scale structure is accompanied by an increase and then a decrease in the structure factor peak near  $q = 0.065 \text{ nm}^{-1}$ . The results in Figs. 2 and 3 hence portray a consistent picture in which the gel that forms at 6.4 C is unstable at the weaker attraction strength and fluidizes only to re-form again later.

This non-monotonic evolution of the gel's rheology, microstructure, and microscopic dynamics following the change in attraction is surprising in light of previous work by Zhang et al.<sup>19</sup> that shows how nanocolloidal suspensions undergoing gel formation and aging in this range of attraction strengths display dynamic scaling in which the suspensions proceed through the apparently same intermediate states with identical rheology, microstructure, and dynamics regardless of the temperature, and only the rate of formation and aging varies. Within this dynamic scaling, a gel that is formed at  $T_i$  and heated to  $T_f$  should be in a state it would have reached if it had formed and aged at  $T_f$  from the beginning (although it would have required longer to reach that state). Hence, one might expect the increase in temperature would only slow, but not reverse, the formation and aging. The observed non-monotonic behavior is instead an example of the Kovacs effect seen in aging glasses<sup>21,22,37-41</sup> and other disordered, out-of-equilibrium materials 40,42-47 that is a manifestation of the

ability of these systems to retain memory.<sup>18</sup> Specifically, the Kovacs effect in an aging glass is the non-monotonic evolution of a quantity like the volume or enthalpy after a succession of two abrupt temperature changes, first a quench through the glass transition temperature to an annealing temperature, and then a smaller jump to a slightly higher final temperature. The second change is often performed when the instantaneous value of the volume or enthalpy coincides with the equilibrium value at the final temperature. Rather than maintain this value, the quantity changes with time before converging back to the equilibrium value. The properties of the gel following the temperature jump similarly converge eventually to those of the gel formed at the higher temperature, as illustrated in Figs. 3(a) and 3(b), which show the evolution of  $g_2(q, \tau = 0.1 \text{ s})$  and I(q) at two wave vectors, respectively, for a gel forming at T = 8.5C along with those from the experiment where the gel is heated from 6.4 to 8.5 C. This convergence is consistent with observations by Gordon et al.<sup>16,48</sup> Overall, the non-monotonic evolution in gel properties following the decrease in attraction strength indicates the gel retains memory of its previous attraction strength, but this memory is transient.

### 2. Transient memory

Non-monotonic behavior following a temperature jump is seen in all measurements with different choices of  $T_i$  and  $T_f$  in which the strength of attraction is lowered ( $\Delta T \equiv T_f - T_i > 0$ ), as long as  $T_f$ is below the gel temperature. For instance, Figs. 4(a) and 4(b) show the temperature profile and the evolution of G', respectively, of the suspension with  $\phi = 0.20$  from measurements where the suspension was quenched to  $T_i = 6$  C and held there for various times  $t_s$  ranging from 600 to 1000 s before heating to  $T_f = 6.8 \text{ C} (\Delta T = 0.8 \text{ C})$ . For comparison, G' as a function of time following a quench directly to 6.8 C is also shown. The behavior follows the same qualitative trends as in Fig. 2(b). At 6 C, G' grows rapidly after a short latency period. After the temperature is increased to 6.8 C, G' first decreases for a time before resuming its growth and eventually converging to the modulus of the suspension quenched directly to 6.8 C. (Similar results for G'' and for the moduli of the suspension with  $\phi = 0.43$ are provided in the supplementary material.) To characterize the convergence, we display in Fig. 4(c) the difference  $\Delta G'$  between the modulus of the gel after the temperature jumps and that of the gel held at 6.8 C throughout as a function of the elapsed time  $\Delta t$  since the temperature becomes stable at 6.8 C. The difference decreases exponentially in time,

$$\Delta G'(\Delta t) = \Delta G'(0) \exp(-\Delta t/\tau_G), \qquad (3)$$

as indicated by the lines, which show the results of fitting Eq. (3) to the data. The convergence times  $\tau_G$  obtained from the fits along with those from measurements with different temperature steps  $\Delta T$  are shown in Fig. 5 as a function of the waiting time prior to the step,  $t_s$ . In each case,  $t_s$  is normalized by the gel time  $t_g$  at  $T_i$  since within the dynamic scaling picture gels at the same  $t_s/t_g$  are in the same mechanical and microscopic state regardless of  $T_i$ .<sup>19,20,34</sup> The convergence time increases approximately linearly with the waiting time and decreases with increasing  $\Delta T$ . These trends are discussed further below.

As further illustration of the non-monotonic behavior in the microscopic dynamics, Figs. 6(a) and 6(b) show the tempera-



**FIG. 4.** (a) Temperature and (b) storage modulus of the suspension with  $\phi = 0.20$  as a function of time from measurements with  $T_i = 6.0$  C,  $T_f = 6.8$  C, and different waiting times. Storage modulus following a quench directly to 6.8 C is shown for comparison. (a) and (b) share the same legend. (c) Difference in G' as a function of time after the temperature became stable at 6.8 C between the three measurements with time-varying attraction and the measurement at 6.8 C throughout. Solid lines are exponential fits to the data.

ture and  $g_2(q,\tau)$  at  $q = 0.068 \text{ nm}^{-1}$  and  $\tau = 0.1$  s, respectively, from XPCS measurements with  $T_i = 6.2$  C,  $T_f = 7$  C, and various  $t_s$ .  $g_2(q,\tau)$  first increases after the initial quench, indicating the system undergoes an ergodic to non-ergodic transition where the particles became increasingly localized. After the attraction is weakened,  $g_2(q,\tau)$  decreases for a time before increasing again and eventually converging to the value of the gel held at 7 C throughout. As with the shear modulus, we characterize this convergence by the difference between the correlation functions measured with time-varying attraction and constant attraction, as illustrated in Fig. 6(c). Again, as with the shear modulus, an exponential decay,



**FIG. 5.** Convergence time of the storage modulus (open) and  $g_2(q, \tau = 0.1 \text{ s})$  at high q (solid) as a function of waiting time normalized by the gel time at  $T_i$  from measurements with different changes in temperature. Dashed line has a slope of 1. Data from all measurements are shown in the supplementary material.



**FIG. 6.** (a) Temperature and (b) correlation function at wave vector  $q = 0.07 \text{ nm}^{-1}$  and delay time  $\tau = 0.1 \text{ s}$  as a function of time from XPCS measurements with  $T_i = 6.2 \text{ C}$ ,  $T_f = 7 \text{ C}$ , and different waiting times. Results from a measurement following a quench directly to 7 C are shown for comparison. (a) and (b) share the same legend. (c) The difference in  $g_2(q, \tau = 0.1 \text{ s})$  between the measurement with  $T_i = 6.2 \text{ C}$ ,  $T_f = 7 \text{ C}$ , and  $t_s = 4200 \text{ s}$  and the measurement at 7 C throughout. Solid line is an exponential fit to the data.

 $\Delta g_2(q, \tau = 0.1 \text{ s}, \Delta t) = \Delta g_2(q, \tau = 0.1 \text{ s}, 0) \exp[-\Delta t/\tau_X(q)], \quad (4)$ 

shown by the line in figure, fits the difference well.

Figure 7 shows the dependence of the convergence time  $\tau_X(q)$ on the wave vector. The convergence time increases with increasing wave vector until about  $q = 0.065 \text{ nm}^{-1}$ , which corresponds to the position of the interparticle structure factor peak of the hard sphere fluid at room temperature, and is almost constant at higher wave vectors. The same trend is observed in other measurements with different  $T_i$  and  $T_f$ , as shown in the supplementary material. This increase in  $\tau_X(q)$  with increasing q at low q indicates that the changes in the gel following the decrease in attraction strength proceed at a rate that is length-scale dependent, with larger-scale microstructural features evolving more quickly than smaller-scale features. At high q,  $g_2(q, \tau)$  at  $\tau = 0.1$  s is in the intermediate plateau whose value reflects the localization length of the particles, which in turn can be related to the elastic modulus.<sup>34-36</sup> This correspondence is reflected in Fig. 5, which shows both  $\tau_X(q)$  at high q and  $\tau_G$ . Note that we limited the times of the temperature steps in the XPCS to larger values than those in the rheology because of the larger thermal equilibration time of the sample in the XPCS experiments. Nevertheless, for the same  $\Delta T$ , the two sets of convergence times fall on a single line as a function of normalized waiting time, indicating a power-law scaling,  $\tau_{(G,X)} \propto (t_s/t_g)^{\delta}$  with exponent  $\delta \approx 1$ . Similar scaling except with  $\delta \approx 0.3$  is observed for the suspension with  $\phi = 0.43$ , as shown in the supplementary material. Furthermore, the dependence of the convergence time on the change in attraction strength can be separated from that on  $t_s$  by introducing a scaled convergence rate  $(t_s/t_g)^{\delta} \tau_{(G,X)}^{-1}$ . Figure 8 shows the scaled convergence rate, which increases exponentially with  $\Delta T$  such that

$$\tau_{(G,X)} \propto (t_s/t_g)^{\delta} \exp(-\xi \Delta T), \qquad (5)$$

with  $\xi = 2.45 \pm 0.12$  and  $1.02 \pm 0.03$  for the suspensions with  $\phi = 0.20$  and 0.43, respectively. Notably, the scaled convergence rates of the shear modulus and microscopic dynamics at  $\phi = 0.20$  collapse



**FIG. 7.** Convergence time of  $g_2(q, \tau = 0.1 \text{ s})$  as a function of wave vector from XPCS measurements with  $T_i = 6.2 \text{ C}$ ,  $T_f = 7 \text{ C}$ , and waiting times specified in the legend.



**FIG. 8.** The scaled convergence rate as a function of the change in temperature from rheology measurements on both the suspensions with  $\phi = 0.20$  and 0.43 and XPCS measurements on the suspension with  $\phi = 0.20$ . Solid and dashed lines are exponential fits to the data at  $\phi = 0.20$  and 0.43, respectively.

in Fig. 8 despite the step times deployed in the experiments differing by more than a factor of 10, further illustrating the connection between the intermediate plateau of the XPCS correlation function and the gel elasticity.

The scaling behavior in Fig. 8 thus suggests a picture of the physics underlying the Kovacs effect in the colloidal gels. At any given strength of attraction, gels pass through a series of agedependent microstates that are unique to that strength of attraction. This uniqueness exists despite the apparent commonality in the properties of aging gels with different attraction strengths revealed by the dynamic scaling.<sup>19</sup> When the strength of attraction is changed, the microstate of the gel is incompatible with the new strength of attraction, and the system is driven toward a new microstate. The microstates associated with different attraction strengths become increasingly divergent as gels ages so that the time required to reach a microstate compatible with a new strength of attraction increases with increasing age. Furthermore, the driving force propelling the evolution from an unstable state to a stable one is larger for larger change in attraction strength, leading to the exponential dependence of the convergence rate on  $\Delta T$ . In Sec. IV, we describe a simple microscopic model to describe aging of colloidal gels that captures the key trends we observe experimentally following a change in attraction.

#### **IV. CLUSTER MODEL**

To better understand the microscopic origins of the transient memory and Kovacs effect, we introduce a model inspired by analytic models for the kinetics of gelation developed by Zaccone *et al.*<sup>13,49</sup> and by the behavior observed in simulations of aging gels by Zia and co-workers.<sup>50</sup> The model considers a system of particles interacting via a step-well attraction with a temperature-dependent depth  $U = ck_B(T_\theta - T)$ , where *c* and  $T_\theta$  are constants, to resemble the interaction of the nanocolloids in the experiments [Eq. (1)]. Each particle is either freely dispersed or in a load-bearing cluster where it bonds with neighbors with a contact number *z* ranging from 1 to 12. Particles continuously join and leave the cluster through attachment and detachment processes, and the contact number determines the rates of attachment and detachment. Specifically, the dynamical equation for the number of particles with contact number z in the cluster is

$$\frac{dn(z,t)}{dt} = K^{+}(z)[N-n(t)] - K^{-}(z,T)n(z,t),$$
(6)

where *N* is the total number of particles,  $n(t) = \sum_{z=1}^{12} n(z,t)$  is the number of particles in the cluster at time *t*, n(z,0) is set to zero for all *z*, and  $K^+(z)$  and  $K^-(z,T)$  are the attachment and detachment rates, respectively. The evolutions of the numbers of particles with different contact number are coupled through the cluster size n(t), since a change in the number of particles with one contact number alters the cluster size, which then affects the exchange balance of particles with other contact numbers. Detachment from the cluster is assumed to be an activated process,

$$K^{-}(z,T) = ae^{-cz(T_{\theta}-T)/T},$$
 (7)

where *a* is a constant, and  $cz(T_{\theta} - T)$  is the bond energy of a particle contacting *z* neighbors. The attachment rates are assumed to be temperature-independent and to have a power-law relation with the contact number to reflect a fractal nature of the cluster, i.e.,

$$K^+(z) = bz^{-d_f},\tag{8}$$

where *b* is a constant, and the fractal dimension is estimated to be  $d_f = 2$ , a value intermediate between those of diffusion-limited and reaction-limited cluster aggregation.<sup>51,52</sup> While the form of Eq. (8) is admittedly arbitrary, we emphasize that the results described below are insensitive to the precise form of  $K^+(z)$ , as long as the attachment rate is a decreasing function of *z*. The mechanical strength of the cluster is estimated by the total bond energy,

$$E(t) = \frac{1}{2} \sum_{z=1}^{12} cz (T_{\theta} - T) n(z, t),$$
(9)

which can be taken as a proxy for the elastic modulus of the gel. Specifically, in a picture in which the gel is composed of particles bonded into load-bearing structures, the shear modulus times a characteristic length set by the particle size *R* should scale as the density of these structures  $\rho$  times the spring constant  $\kappa$  characterizing the bonds,  $G'R \sim \rho\kappa$ . Furthermore, if the density of load-bearing structures scales with the density of contacts,  $\rho = \sum_{z=1}^{12} zn(z,t)/2V$ , where *V* is the volume, then  $G' \sim \kappa \sum_{z=1}^{12} zn(z,t)/2RV$ , or  $G' \sim E\kappa/(2RVc(T_{\theta} - T))$ .<sup>53</sup>

The temporal evolution of the cluster is acquired by iteratively evaluating Eq. (6) using parameters a = 1, b = 0.01, c = 14,  $T_{\theta} = 33$  C, and  $N = 10^4$ . Again, the precise values of these parameters are unimportant in dictating the qualitative forms of n(z, t) and E(t). The temperature is set to an initial value  $T_i$  at the beginning and instantly raised to a final value  $T_f$  after a certain number of time steps to mimic the experiments. We recognize that this model is a severe

over-simplification of gel formation and aging, and, in particular, it neglects factors such as the effect that adding a particle to the cluster has on the contact number of those to which it attaches and the fact that high *z* particles would typically reside in the interior of the cluster making them even less susceptible to detachment than suggested by Eq. (7). Nevertheless, as shown below, the model reproduces qualitative trends seen in the experiments, including the transient memory displayed by the gels.

Figure 9 shows the cluster size as a function of time with  $T_i$  = 3 C, raised to  $T_f$  = 10 C after various time steps. Also shown is the cluster size when the temperature is kept at 10 C throughout. At the initial temperature, an imbalance between attachment and detachment drives steady growth of the cluster. At higher attraction strength, the detachment rates are smaller at all contact numbers, so the cluster not only grows faster, as seen in Fig. 9, but also approaches a larger final size at long time, as shown in the supplementary material. After the change in temperature, the cluster size first decreases, then gradually regains growth, and eventually converges to the size of the cluster held at 10 C throughout. Thus, the cluster size displays a non-monotonic time dependence following a decrease in attraction strength similar to those seen experimentally in G',  $g_2(q,\tau)$ , and I(q). As shown in the inset to Fig. 9, the cluster energy also has a non-monotonic, converging evolution. Additional results are shown in the supplementary material.

The transient memory of the original attraction strength can be quantified by the difference  $\Delta n$  between the cluster size in the cases where the temperature is varied and where it is kept constant. As shown in Fig. 10(a), this difference decreases until it reaches a minimum below zero and then converges to zero from below. Thus, the convergence of the cluster size is more complicated than the simple exponential convergence seen in the experiments. The difference in the cluster energy also shows a negative minimum and converges to zero from below as shown in the supplementary material. To characterize the time scale of this convergence, we show in the



**FIG. 9.** Cluster size as a function of time step where the temperature is increased from 3 to 10 C after different time steps as specified in the legend. The cluster size at 10 C throughout is shown for comparison. Inset: Energy of the cluster as a function of time step where the temperature was increased to 10 C after 3000 time steps at 3 C compared to the energy of a cluster kept at 10 C.



**FIG. 10.** (a) The difference in size between model clusters where the temperature is raised to 10 C from 3 C after different time steps as specified in the legend and a cluster kept at 10 C as a function of time step after the change in temperature. Inset: Time steps to reach the minimum difference in cluster size (circles) and energy (squares) after the change in temperature as a function of time spent at the initial temperature. The solid line shows a power law with exponent 0.3. (b) The cluster size as a function of time step where the temperature is raised to different values as specified in the legend after 4000 steps at 2 C. Sizes of clusters kept at corresponding fixed temperatures are shown as lines for comparison. Inset: the time to reach minimum difference in cluster size (circles) and energy (squares) as a function of the change in temperature.

inset to Fig. 10(a) the number of time steps  $\tau_{\min}$  to reach the minimum of  $\Delta n$  and  $\Delta E$  as a function of the number of time steps  $t_s$  spent at the initial strength.  $\tau_{\min}$  increases with  $t_s$  as a weak power law,  $\tau_{\min} \sim t_s^{\delta}$  with  $\delta = 0.3$ , matching the trend seen experimentally for G' at  $\phi = 0.43$ .

While this agreement between the model and the experimental results for  $\phi = 0.43$  is intriguing, we note that the gel density is not specified in the model, and further the model contains nothing about spatial correlations among bonds. Therefore, the better agreement for  $\tau_{\min}$  vs  $t_s$  between the model and the suspension with  $\phi = 0.43$  as opposed to  $\phi = 0.20$  could simply be a coincidence. On the other hand, the model in some sense provides a mean-field picture, and one might expect such a picture better captures higherconcentration gels that are less spatially heterogeneous. Regardless, the significance of the model results is less in the quantitative details than in the success in capturing qualitatively the trends seen at both concentrations. Figure 10(b) shows the evolution of the cluster size in the case where  $T_i = 2$  C and the temperature is raised to various final temperatures after 4000 time steps. The inset to Fig. 10(b) shows the corresponding convergence times, which decrease with increasing change in temperature  $\Delta T$  approximately exponentially like in the experiments. The model thus also successfully recovers the scaling of the convergence time with  $\Delta T$  seen experimentally.

The origin of the non-monotonic behavior in the model can be identified by examining the dependence of n(z, t) on z. This distribution in contact number, which has provided unique perspectives <sup>54–59</sup> varies in previous studies on the gelation of colloidal systems,<sup>5</sup> with the attraction strength and with age and serves as a signature of the gel's microstate. Figure 11(a) shows the contact number distributions at different time steps at 3 and 10 C. On one hand, the distribution at fixed attraction gradually shifts to higher z with time, resembling gel coarsening during aging observed in simulation.<sup>50</sup> On the other hand, as shown in Fig. 11(c), at any given time, the cluster with higher attraction strength has an excess of low z particles and a deficit of high z particles compared to that with lower attraction, and the difference becomes more pronounced at high z with increasing t. After the strength of attraction is decreased, the new detachment rates lead the cluster to evolve so that the distribution of contact numbers converges to that of the system kept with at the weaker attraction throughout, as illustrated in Fig. 11(b), which shows the distributions of a system heated from 3 to 10 C after 1000 time steps and the one kept at 10 C throughout. The distributions are essentially identical by 16 000 time steps (15 000 time steps after the temperature jump). Significantly, however, the rates at which the populations of different contact numbers converge depends on the contact number. Figure 11(d) shows the difference in distributions of contact number between a cluster heated to 10 from 3 C at time step 1000 and one with the temperature fixed 10 C. The differences are largely positive and decay faster in low z region, which results in the decrease in cluster size after the weakening of attraction, while the negative differences at high z region decay slowly and lead to the undershoot of cluster size seen in Figs. 9 and 10(a). This *z*-dependent relaxation can be clearly seen in Fig. 11(e), which shows the difference  $\Delta n(z)$ , normalized by the magnitude of the difference immediately before the temperature change, as a function of time after the temperature change. These positive differences at low z and negative differences at high z become more pronounced with increasing temperature difference, as illustrated in Fig. 11(f).

The origin of the Kovacs effect in the aging gels can be identified with the dynamic heterogeneity in  $\Delta n(z)$  at different z seen in Fig. 11(e). Specifically, the populations of particles with small z respond relatively quickly to the change in temperature, and since  $\Delta n(z)$  is positive for small z, this leads to the initial decrease in *n* and *E*. At later times, the change is population at high z becomes important, and since  $\Delta n(z)$  is negative at high z, n and E increase. Previous models to explain the Kovacs effect in glasses and other disordered systems have invoked similar explanations in which two sets of degrees of freedom dictating a property of the system evolve in opposite ways and act on different time scales to produce the non-monotonic response.<sup>3</sup> While in some models the distribution of relaxation times is simply phenomenological, here we have a concrete microscopic picture for them in the particle bonding in the gel with various contact number.



**FIG. 11.** (a) Distributions of contact number of clusters at 3 C (open) and 10 C (solid) at various time steps as specified in the legend. (b) Distributions of contact number at different time steps where the temperature was heated to 10 from 3 C (open) at time step  $t_s = 1000$ . The distributions of a cluster kept at 10 C (solid) are shown for comparison. (c) The difference in the distribution of contact number between the two systems shown in (a) at different time steps. (d) The difference in the distribution of contact number between the two systems shown in (a) at different time steps. (d) The difference in the distribution of contact number between the two systems shown in (b) at different time steps. (e) The difference in the numbers of particles with different contact number between the cluster stepped from 3 to 10 C and the cluster kept at 10 C as a function of time step after the change in temperature. The difference is normalized by the magnitude of the difference immediately before the change in temperature. (f) Difference in the distribution of contact number at time step 2000 between clusters at various fixed temperatures as specified in the legend and a reference cluster at 10 C.

# V. CONCLUSION

These experiments on gel formation and aging of nanocolloidal suspensions with time-varying attraction have revealed unexpected phenomena. Most striking is the temporary reversion of the aging process following a decrease in attraction strength, which can be so significant that it leads to return of the suspension into a fluid and subsequent re-formation of the gel. This reversion indicates that gels formed at even modestly different strengths of attraction have distinct and mutually incompatible microstructures despite their strongly similar properties.<sup>19</sup> This fact, combined with the out-of-equilibrium nature of the gel state, enables the gels to display a memory of the strength of attraction that our work has revealed.

An interesting extension of this study would be to examine aging gels' response to other time variations in the strength of

attraction. Experiments on spin glasses and structural glasses with different temperature protocols, such as stepping back and forth between two temperatures below the glass transition<sup>64-67</sup> or cooling and re-heating with temporary interruptions,68,69 have uncovered other striking realizations of memory in these systems that have provided insight into their out-of-equilibrium state. Memory effects similar to those seen in spin glasses on temperature cycling have also been reported for a gelatin gel.<sup>70</sup> We further note that the convergence of the properties of the gel following an upward temperature step to those of the gel maintained at the higher temperature indicates that the gel formation has characteristics of an equilibrium thermal process, as noted previously.<sup>16</sup> Whether such converging behavior persists under different other time-variation protocols or following initial quenches to lower temperature, which potentially access different regimes of gel formation,<sup>31</sup> would be an interesting test of this idea. As a first step in expanding the current work, we have performed measurements on the colloidal gels in which we introduce downward temperature steps  $(T_f < T_i)$  to suddenly increase the strength of attraction during aging. A brief report on some of these results is provided in the supplementary material.

The simple cluster model that reproduces the non-monotonic time dependence of the Kovacs effect in the gels provides further insights into the gel formation and aging processes. The key feature underlying the effect is structure-related dynamic heterogeneity, represented in the model by the contact-number-dependent exchange rates that lead to a relaxation spectrum with longer decay times at higher contact number. Recently, the contact number distribution has been a point of focus in studying gelation and other properties of colloidal gels,<sup>50,54-59</sup> and one can expect the assumptions and results of the model could be tested in future experiments with confocal microscopy<sup>55</sup> and simulations.<sup>50</sup> Also, one can imagine that a different parameter besides contact-number distribution might be the relevant microstructural feature whose dispersive relaxation rate underlies the Kovacs effect. An alternative candidate could be the relative population of different "locally favored structures" that have been identified as the primary building blocks of percolating gel networks.<sup>11</sup> Overall, the approach presented here of tunably varying attraction strength opens a new perspective for understanding the mechanisms of colloidal gel formation and aging and its relation to other out-of-equilibrium systems in nature.

# SUPPLEMENTARY MATERIAL

See the supplementary material for the additional results mentioned in the text earlier.

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### AUTHOR DECLARATIONS

#### **Conflict of Interest**

The authors have no conflicts to disclose.

### **Author Contributions**

Yihao Chen: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). Qingteng Zhang: Conceptualization (equal); Data curation (equal); Investigation (equal); Methodology (equal); Writing – review & editing (equal). Subramanian Ramakrishnan: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Writing – review & editing (equal). Robert L. Leheny: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal).

### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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average particle localization length, and  $z_{avg} = \frac{1}{N} \sum_{z=1}^{12} zn(z, t)$  is the average contact number. Noting further that  $E = Nc(T_{\theta} - T)z_{avg}/2$ , when combined with  $G' \sim E$ , leads to the familiar result  $G'a \sim k_B T r_{loc}^{-2.35}$ 

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