When gel and glass meet: A mechanism for multistep relaxation

Pinaki Chaudhuri,[1] Ludovic Berthier,[2] Pablo I. Hurtado,[3] and Walter Kob[2]

[1]*Laboratoire PMCN, Université Lyon 1, UMR CNRS 5586, Université de Lyon, 69622 Villeurbanne, France*

[2]*Laboratoire des Colloïdes, Verres et Nanomatériaux, UMR CNRS 5587, Université Montpellier 2, 34095 Montpellier, France*

[3]*Instituto Carlos I de Física Teórica y Computacional, Universidad de Granada, Granada 18071, Spain*

We use computer simulations to study the dynamics of a physical gel at high densities where gelation and the glass transition interfere. We report and provide detailed physical understanding of complex relaxation patterns for time-correlation functions which generically decay in a three-step process. For certain combinations of parameters we find logarithmic decays of the correlators and subdiffusive particle motion.

PACS number(s): 61.20.Lc, 61.43.Bn, 82.70.Gg

Various types of phase transformations in disordered materials have been described in the literature, such as percolation, gelation, or glass transition [1]. It is thus natural to seek novel behaviors emerging from the competition between these different transformations. Recently, the structure and dynamics of mixtures of large and small colloidal particles [2,3] of materials with competing length scales [4,5] or interactions [6–8] have been studied using a variety of theoretical and experimental techniques. The motivation to carry out these investigations is of fundamental as well as practical nature since new phenomena can be discovered and disordered materials with novel properties are created.

Of particular interest are the similarities, differences, and competition between gelation and glass transition which can be observed in a number of soft materials [9–12]. Previous work focused on particle systems with a hard-core repulsion competing with a very short-range attraction [6], which can be realized experimentally in colloid-polymer mixtures [11]. Such systems can be handled theoretically using liquid state theory for the structure, and mode-coupling theory for the dynamics, which then yields detailed predictions for the location and nature of the dynamic transitions [6,13]. Nonergodic phases are predicted either upon compression (glass physics) or upon increasing the attraction strength (gelation), with a peculiar dynamical behavior (logarithmic decay of time-correlation functions and subdiffusive particle displacements) in the region of parameter space where these transition lines intersect. A number of confirmations have been obtained [6,10–12,14–16].

However, the competition between gel and glass is not restricted to sticky particles, and an exploration of a larger class of materials is needed. Additionally, a detailed physical understanding of the competition between these two forms of dynamic arrest has not been achieved. Also, since mode-coupling singularities are generically avoided in real materials [1], it is important to explore the robustness or generality of the above results [17], and the possible deviations or new processes which might emerge when a larger class of materials is considered.

We explore these important open directions using simulations of a model system that is a coarse-grained representation [18] of a transient gel which has been studied in experiments [19]. In this system an equilibrium low-density gel is obtained by adding telechelic polymers to an oil-in-water microemulsion. Since the polymer end groups are hydropho-

bic, the polymers effectively act as (attractive) bridges between the oil droplets they connect, whose strength, length scale and typical lifetime can be controlled at will. Denoting by C_{ij} the number of polymers connecting droplets i and j, we have established in Refs. [18,20] that the following interaction is an effective coarse-grained representation of this ternary system:

$$V = \sum_{j>i} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{14} + \epsilon_1 \sum_{j>i} C_{ij} V_{\text{FENE}}(r_{ij}) + \epsilon_0 \sum_i C_{ii}. \quad (1)$$

The first term is a soft repulsion acting between bare oil droplets, where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, σ_i is the diameter of droplet i, and r_{ij} is the distance between droplet centers. The second term describes the entropic attraction induced by the telechelic polymers, which has the standard "FENE" form (finitely extensible nonlinear elastic potential) known for polymers [21], $V_{\text{FENE}} = \ln(1 - (r_{ij} - \sigma_{ij})^2/\ell^2)$, and accounts for the maximal extension ℓ of the polymers. The last term introduces the energy penalty ϵ_0 for polymers that have both end groups in the same droplet. The most drastic approximation of model (1) is the description of the polymers as "bonds" between the droplets, which is justified whenever the typical bond lifetime is much larger than the time scale for polymer dynamics in the solvent [19]. To describe the dynamics of the system, we combine molecular dynamics to propagate the droplets with interaction (1) to local Monte Carlo moves with Metropolis acceptance rates $\tau_{\text{link}}^{-1} \min[1, \exp(-\Delta V/k_B T)]$ to update the polymer connectivity matrix C_{ij} [18,20]. Thus τ_{link} is the time scale governing the renewal of the polymer network topology. In order to prevent crystallization we use a polydisperse emulsion with a flat distribution of particle sizes in the range $\sigma_i \in [0.75, 1.25]$.

For moderate volume fraction, $\phi \approx 0.2$, the model behaves as an equilibrium transient gel with nontrivial dynamics [18] if R, the fraction of polymers per oil droplet, is larger than the percolation threshold $R_p \approx 2$. In this case, the system is viscoelastic with a relaxation time set by the bond lifetime τ_{link}, and mechanical strength set by R, as illustrated in Fig. 1(a) where we show the time dependence of the self-intermediate scattering function,
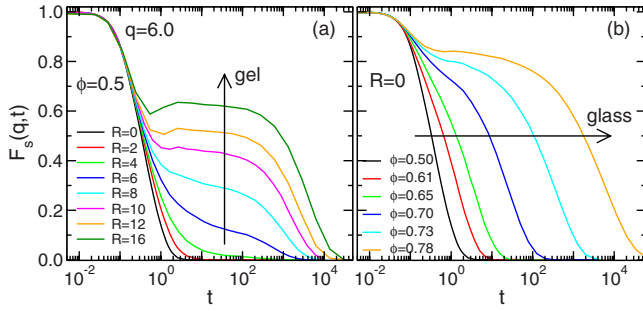
FIG. 1. (Color online) Time dependence of $F_s(q,t)$ for $q=6.0$. (a) Gelation at $\phi=0.5$, $\tau_{link}=10^2$, and increasing R. (b) Glass transition at $R=0$ and increasing ϕ.

$$F_s(q,t) = \frac{1}{N}\sum_j \exp(i\mathbf{q}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]), \qquad (2)$$

across percolation for $\phi=0.5$ ($q=6.0$, near the main peak in the static structure factor). A two-step decay is observed with a plateau height controlled by R, and a slow decay at times $t\approx\tau_{link}$. These features reflect the vibrations of an increasingly stiffer network of connected particles, followed by a slow reorganization of the transient network. In the opposite limit where $R=0$ and the volume fraction ϕ becomes large, the microemulsion becomes a standard dense glass [Fig. 1(b)]. Here, the two-step decay stems from particle vibrations within the transient cage formed by the neighbors, followed by slow structural relaxation. As usual in this situation, the relaxation time increases dramatically with ϕ while the plateau height remains constant [1].

Our goal in this work is to explore the competition between the two well-documented phenomena illustrated in Fig. 1. The space of control parameters is large, so we fix [18] $\{\ell=3.5,\ k_BT=\epsilon_0=1,\ \epsilon_1=50\}$ and vary $\{\phi,R,\tau_{link}\}$. We successively describe the effect of (i) increasing the density of an equilibrium gel, (ii) adding attractive interactions to a viscous liquid close to the glass transition, and (iii) changing the bond lifetime of a system close to dynamic arrest to estimate the relative importance of bonding and steric hindrance for the relaxation.

We start our exploration in Fig. 2 which shows the evolution of the equilibrium gel dynamics, $R=8$, $\tau_{link}=10^2$, as it is compressed from $\phi=0.5$ toward the glass transition. Contrary to the extreme cases shown in Fig. 1, here both the relaxation time and the plateau height increase simultaneously. Thus these results are not explained by gelation or the glass transition alone but truly result from the nontrivial effect of their competition. This is directly demonstrated by increasing, for the same state points, the bond lifetime τ_{link} to a very large value. For $\phi=0.5$, the correlator quickly decays to the plateau and then becomes completely arrested, showing that at low density only the transient network physics is at play. At larger density, $\phi=0.60$ and 0.65, a very slow decay toward a plateau is observed. In particular, for $\phi=0.65$ the data follow a nearly logarithmic decay over about 5 decades in time, a behavior which is seen neither for the gel nor the glass alone. This means that the elastic relaxation of the network is considerably slowed down by crowd-
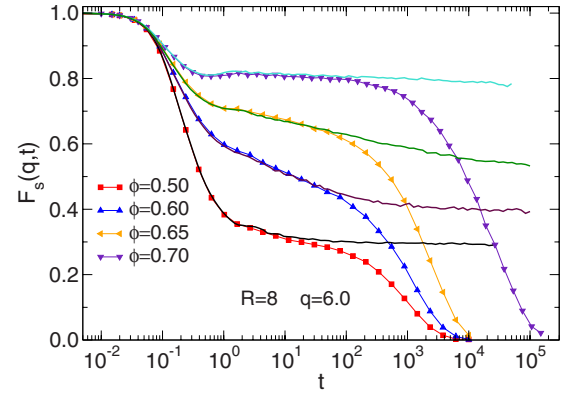

FIG. 2. (Color online) Compressing an equilibrium transient gel with $R=8$ toward the glass transition. The symbols are for $\tau_{link}=10^2$ and the full lines are for frozen bonds, $\tau_{link}=\infty$. The dynamical evolution is a nontrivial mixture of both gelation and glass transition with a logarithmic decay toward a plateau at intermediate volume fraction.

ing effects. Interestingly, qualitatively similar experimental observations have recently been reported in micelles [12] and attractive nanoparticles [16]. At even larger volume fractions, $\phi=0.7$, $F_s(q,t)$ decays again in a two-step process, but the slow decay is now controlled both by the bond lifetime (as in gels) and by the density (as glassy liquids). Although the dynamics at large ϕ and R is a two-step process similar to the one of the glassy fluid at $R=0$, the effect of τ_{link} on the second decay establishes its very different nature. While crowding alone is responsible for the slow dynamics near $R=0$, bond lifetime and network reorganization control the dynamics at large R. This physical distinction is reminiscent of the "bonded glass" and "repulsive glass" nomenclature introduced for attractive colloids [22]. It is between these two regimes that multistep relaxations can be observed.

Alternatively, gel and glass can meet by increasing the attraction in dense systems, as usually done in polymer-colloid mixtures [11,14]. Note that in our model we can increase the attraction between droplets, R, without simultaneously increasing the bond lifetime τ_{link}, while these quantities are tightly coupled in attractive colloids [11,14,15]. This allows us to disentangle static from dynamic effects. In Fig. 3 we show the effect of increasing R in a dense fluid at $\phi=0.61$ using a constant bond lifetime $\tau_{link}=10^2$. We show both the evolution of $F_s(q,t)$, and of the mean-squared displacement,

$$\Delta^2(t) = \frac{1}{N}\sum_i \langle|\mathbf{r}_i(t)-\mathbf{r}_i(0)|^2\rangle. \qquad (3)$$

As for the low-density system in Fig. 1, increasing the attractive interaction allows the system to cross the percolation line and to become viscoelastic; i.e., $F_s(q,t)$ decays in two steps. However, the proximity of the glass transition makes the dynamic evolution more complex, as this produces, at intermediate values of $R\approx5-7$ a very slow decay of the time-correlation function, which can be empirically described by a logarithmic decay [Fig. 3(a)]. This behavior resembles the ones reported in numerical work for colloids
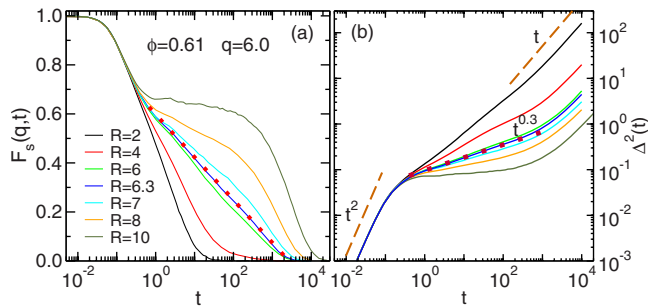
FIG. 3. (Color online) Effect of increasing the attractive interactions, R, in a dense repulsive fluid, $\phi=0.61$, for a finite bond lifetime, $\tau_{link}=10^2$ on (a) $F_s(q,t)$ and (b) $\Delta^2(t)$. For intermediate R values, a nearly logarithmic time decay of $F_s(q,t)$ is observed (symbols), associated with a subdiffusive behavior of single-particle displacements.

with short-range attraction [14,15]. The mean-squared displacement also evidences deviations from a simple two-step process, as particle displacements appear to be transiently subdiffusive at those intermediate R where logarithmic decay is observed. Again this behavior cannot be accounted for by a simple "superposition" of gel and glass dynamics.

We explore further these nontrivial dynamical features making use of the flexibility offered by the present model to change attraction and bond lifetime independently. In Fig. 4, we show the effect of increasing τ_{link} on $F_s(q,t)$ and $\Delta^2(t)$ for constant values of $R=6.3$ and $\phi=0.61$, i.e., where the logarithmic decay was most prominent in Fig. 3. We now realize that the logarithmic decay seen for $\tau_{link}=10^2$ is in fact a very specific instance of a more generic three-step decay of time-correlation functions which reflects the double localization of the particles within their cages and within the transient particle network. This three-step process is also clear from the behavior of the mean-squared displacements (inset of Fig. 4), which reveals the existence of two length scales controlling the dynamics of this system. A first plateau is observed for $\Delta^2 \approx 0.1$, which corresponds to the typical cage size in repulsive glasses [1], and a second plateau is observed near
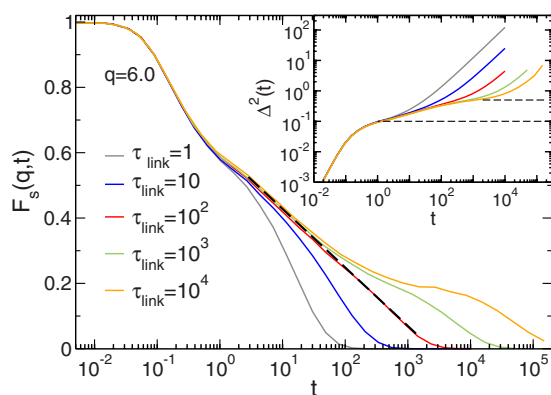

FIG. 4. (Color online) Increasing the bond lifetime τ_{link} from 1 to 10^4 at $\phi=0.61$ and $R=6.3$ produces a crossover from nearly logarithmic (dashed line) to a three-step process when time scales are well separated. The inset shows the mean-squared displacement for the same parameters, revealing the existence of the distinct length scales (dashed lines) controlling the dynamics.
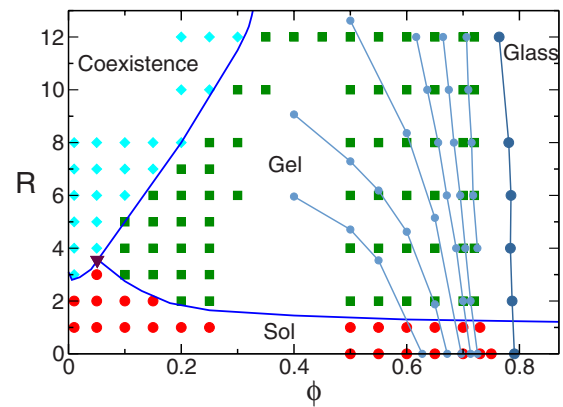

FIG. 5. (Color online) Phase diagram for $\tau_{link}=1.0$: Coexistence region ($\diamond$), sol ($\bigcirc$) and gel ($\square$) phases, and measured glass line ($\triangle$), determined from a Vogel-Fulcher fit of the relaxation time. Also shown are the iso-τ lines ($\triangledown$) for $\tau=10, 30, 10^2, \ldots, 10^4$.

$\Delta^2 \approx 0.5$, which corresponds to the localization of the particle due to the presence of the percolating polymer network [18]. The logarithmic decay is only observed if a nongeneric combination of time scales and length scales combines both slow processes in a single, nearly logarithmic one. In fact our data suggest that the *generic* situation should be the occurrence of a three-step process corresponding to well-separated bond/cage relaxation. To the best of our knowledge, there is no experimental report of such a three-step decay of time-correlation function. We suggest that compressing the transient gel system of Ref. [19] is a possible route to such observations.

We now summarize our findings in a phase diagram in Fig. 5. The low-density part, $\phi<0.2$, was described earlier [18]. It contains a sol phase if ϕ and R are small, and a phase separated region when attraction is increased at low ϕ. There is a large region (currently explored in experiments [19,23]) where a homogeneous equilibrium transient gel is formed. In the present work we have explored the interplay between the glass transition at large volume fraction and gelation at large R, where we observed interesting dynamical phenomena. The isorelaxation-time lines reported in Fig. 5, obtained for $\tau_{link}=1.0$ and defined by $F_s(q,\tau)=0.03$, show that the dynamics slows down both by increasing ϕ or R [24]. In the region where both R and ϕ act as a source for slow dynamics we generically obtain a three-step relaxation process, which produces for specific combinations of R, ϕ, and τ_{link}, a logarithmic decay toward a plateau followed by a slower decay, as in Fig. 2, or a fully logarithmic decay as in Fig. 3. The present model thus captures a broad range of behaviors, and also predicts new types of relaxations.

The phase diagram in Fig. 5 shows that, in the gel phase, ergodic behavior is found even if the attraction gets very large. For $\phi=0.5$, we have done simulations up to $R=50$ and still found ergodic behavior: the relaxation time increasing smoothly with R. Thus we find no evidence of an "ideal" gel phase, as predicted theoretically for attractive particles [6,13,25], although of course the relaxation time can get very large if both R and τ_{link} increase. This suggests a fundamental difference between gelation and glass transition because

in (fragile) glass-forming materials, the predicted mode-coupling singularity is also avoided, but it is believed to be replaced by a truly divergent time scale [1]. As suggested also from simulations of particles with attractive patches [8], gels could be the analog of Arrhenius (strong) glasses with no finite temperature singularity.

One important finding of our study is the prediction of a generic three-step decay of time-correlation functions, which has not yet been directly observed experimentally. As shown in Fig. 4, this requires the existence of two distinct length scales and well-separated time scales for cage/bond relax-

ation. We suggest that the observation of a two-step process for yielding in a sheared colloid-polymer mixture [26] might be a rheological analog of Fig. 4, which certainly calls for further investigations. Even more complex relaxation dynamics could potentially emerge in transient gels made with polymer mixtures having distinct length scales, thus opening the door to the creation of new materials.

---

[1] K. Binder and W. Kob, *Glassy Materials and Disordered Solids* (World Scientific, Singapore, 2005).

[2] A. Imhof and J. K. G. Dhont, Phys. Rev. Lett. **75**, 1662 (1995).

[3] A. J. Moreno and J. Colmenero, J. Chem. Phys. **125**, 164507 (2006).

[4] A. J. Moreno and J. Colmenero, Phys. Rev. E **74**, 021409 (2006).

[5] M. Sperl, E. Zaccarelli, F. Sciortino, P. Kumar, and H. Eugene Stanley, Phys. Rev. Lett. **104**, 145701 (2010).

[6] A. M. Puertas and M. Fuchs, in *Structure and functional properties of colloidal systems*, edited by R. Hidalgo-Alvarez (Taylor and Francis, London, 2009).

[7] M. Bernabei, A. J. Moreno, and J. Colmenero, Phys. Rev. Lett. **101**, 255701 (2008).

[8] E. Zaccarelli, I. Saika-Voivod, S. V. Buldyrev, A. J. Moreno, P. Tartaglia, and F. Sciortino, J. Chem. Phys. **124**, 124908 (2006).

[9] D. Bonn, H. Kellay, G. Wegdam, and J. Meunier, Langmuir **15**, 7534 (1999).

[10] T. Eckert and E. Bartsch, Phys. Rev. Lett. **89**, 125701 (2002).

[11] K. N. Pham, A. M. Puertas, J. Bergenholtz, S. U. Egelhaaf, A. Moussaid, P. N. Pusey, A. B. Schofield, M. E. Cates, M. Fuchs, and W. C. K. Poon, Science **296**, 104 (2002).

[12] S. H. Chen, W. R. Chen, and F. Mallamace, Science **300**, 619 (2003).

[13] K. Dawson, G. Foffi, M. Fuchs, W. Götze, F. Sciortino, M. Sperl, P. Tartaglia, T. Voigtmann, and E. Zaccarelli, Phys. Rev.
E **63**, 011401 (2000).

[14] A. M. Puertas, M. Fuchs, and M. E. Cates, Phys. Rev. Lett. **88**, 098301 (2002).

[15] F. Sciortino, P. Tartaglia, and E. Zaccarelli, Phys. Rev. Lett. **91**, 268301 (2003).

[16] X. H. Lu, S. G. J. Mochrie, S. Narayanan, A. R. Sandy, and M. Sprung, Phys. Rev. Lett. **100**, 045701 (2008).

[17] P. L. Geissler and D. R. Reichman, Phys. Rev. E **71**, 031206 (2005).

[18] P. I. Hurtado, L. Berthier, and W. Kob, Phys. Rev. Lett. **98**, 135503 (2007).

[19] E. Michel, M. Filali, R. Aznar, G. Porte, and J. Appell, Langmuir **16**, 8702 (2000).

[20] P. I. Hurtado, P. Chaudhuri, L. Berthier, and W. Kob, AIP Conf. Proc. **1091**, 166 (2009).

[21] T. A. Witten, *Structured Fluids* (Oxford University Press, Oxford, 2004).

[22] E. Zaccarelli and W. C. K. Poon, Proc. Natl. Acad. Sci. U.S.A. **106**, 15203 (2009).

[23] H. Tabuteau, S. Mora, G. Porte, M. Abkarian, and C. Ligoure, Phys. Rev. Lett. **102**, 155501 (2009).

[24] No "re-entrance" of the glass line should be expected for the present system, as the range of the attraction, set by the polymer length, ℓ, is too large [13].

[25] J. Bergenholtz and M. Fuchs, Phys. Rev. E **59**, 5706 (1999).

[26] K. N. Pham, G. Petekidis, D. Vlassopoulos, S. U. Egelhaaf, P. N. Pusey, and W. C. K. Poon, Europhys. Lett. **75**, 624 (2006).