When gel and glass meet: A mechanism for multistep relaxation

Pinaki Chaudhuri,1 Ludovic Berthier,2 Pablo I. Hurtado,3 and Walter Kob2

1Laboratoire PMCN, Université Lyon 1, Université de Lyon, UMR CNRS 5586, 69622 Villeurbanne, France
2Laboratoire des Colloïdes, Verres et Nanomatériaux, UMR CNRS 5587, Université Montpellier 2, 34095 Montpellier, France
3Instituto Carlos I de Física Teórica y Computacional, Universidad de Granada, Granada 18071, Spain

(Dated: November 27, 2009)

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 numbers: 61.43.Bn, 82.70.Gg, 61.20.Lc

Various types of phase transformations in disordered materials have been described in the literature, such as percolation, gelation, or glass transition [1], and it is thus natural to seek novel behaviors that emerge 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 of systems with competing interactions [6,7] has 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 [8,9,10,11]. 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 [10]. 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 [6,12]. Non-ergodic solids are predicted both upon compression (glass physics) or upon increasing the attraction strength (gelation), with a peculiar dynamical behavior (logarithmic decay of time correlation functions and sub-diffusive particle displacements) in the region of parameter space where these transition lines intersect. A number of numerical simulations [6,13,14] and experiments [9,10,11,17] have confirmed the overall topology of the phase diagram, with some simulations reporting the dynamical signatures predicted theoretically [13,14]. However, a detailed physical understanding of these dynamics and an exploration of their universality for more complex materials has not been achieved. Moreover, since mode-coupling singularities are generically avoided in real materials [11], it is important to explore also the robustness or generality of these results [16], and the possible deviations or new processes which might emerge in real materials.

We explore these important open directions using computer simulations of a model system that is a coarse-grained representation [17] of a transient gel which has been studied in experiments [18]. 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 hydrophobic, the polymers effectively act as (attractive) bridges between the oil droplets they connect, whose strength, lengthscale 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. [17,19] that the following interaction is an effective coarse-grained representation of this ternary system:

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

The first term is a soft repulsion acting between bare oil droplets, where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, $\sigma_i$ is the diameter of droplet $i$, and $r_{ij}$ is the distance between the droplet centers. The second term describes for the entropic attraction induced by the telechelic polymers, which has the standard “FENE” form known from polymer physics [20], $V_{\text{FENE}}(r_{ij}) = \ln(1 - (r_{ij} - \sigma_{ij})^2/\ell^2)$, and accounts for the maximal extension $\ell$ of the polymers. The last term introduces the energy penalty $\epsilon_0$ for polymers that have both end-groups in the same droplet. The most drastic approximation of the model [11] is the description of the polymers as effective bonds between the droplets, which is justified whenever the typical lifetime of the bonds is much larger than the timescale for polymer dynamics in the solvent [18]. In order to describe the dynamics of the system, we use a combination of molecular dynamics to propagate the droplets with the interaction (1), and 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 $C_{ij}$ \cite{17, 19}. Thus $\tau_{\text{link}}$ is the timescale 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 non-trivial dynamics \cite{17} 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 $\tau_{\text{link}}$, and mechanical strength set by $R$, as illustrated in Fig. 1 where we show the time dependence of the self-intermediate scattering function.

\[
F_s(q, t) = \frac{1}{N} \sum_j \exp(iq \cdot (r_j(t) - r_j(0))),
\]

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 $t \approx \tau_{\text{link}}$. 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 $\phi$ becomes large, the microemulsion becomes a standard dense glass, Fig. 1b. 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 $\phi$ while the plateau height remains constant \cite{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 \cite{17} \{\[\ell = 3.5, k_B T = \epsilon_0 = 1, \epsilon_1 = 50\]\} and vary $\{\phi, R, \tau_{\text{link}}\}$. We successively describe the effect of (i) increasing the density of an equilibrium gel, (ii) adding attractive interactions to a viscous close to the glass transition, (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, $R = 8$, $\tau_{\text{link}} = 10^2$, as it is compressed from $\phi = 0.5$ towards 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 non-trivial effect of their competition. This is directly demonstrated by increasing, for the same state points, the bond lifetime $\tau_{\text{link}}$ 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 towards 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 crowding effects. Interestingly, qualitatively similar experimental observations have recently been reported in micelles \cite{11} and attractive nanoparticles \cite{12}. 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 density (as glassy liquids). Although the dynamics at large $\phi$ and $R$ is a two-step process similar to the one of the glassy fluid at $R = 0$, the effect of $\tau_{\text{link}}$ 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 intro-
Intermediate moments appear to be transiently sub-diffusive at those in-
creased values of \( \tau_{\text{link}} \) which yields a near logarithmic decay.
This behavior resembles the ones reported in numerical
experiments [18, 22] where a homogeneous, equilibrium, transient gel is formed. In the present work we have ex-
plored the interplay between the glass transition at large volume fraction and gelation at large \( R \), where we dis-
covered new dynamical phenomena. The iso-relaxation
stant values of \( R = 6.3 \) and \( \phi = 0.61 \), i.e. where the log-
arithmetic decay was most prominent in Fig. 3. We now
realize that the logarithmic decay seen for \( \tau_{\text{link}} = 10^2 \)
is in fact a very specific instance of a more generic
three-step decay of time correlation functions which re-
ffects 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 re-
veals the existence of two lengthscales 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 re-
wpulsive glasses [1], and a second plateau is observed near
\( \Delta^2 \approx 0.5 \), which corresponds to the localization of the
particle due to the presence of the percolating polymer
network [17]. The logarithmic decay is only observed if a
non-generic combination of timescales and lengthscales
combines both slow processes in a single, nearly logarith-
mic one. In fact our data suggest that the generic situa-
tion should be the occurrence of a three-step process cor-
responding 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. [18] 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 ear-
lier [17]. It contains a sol phase if \( \phi \) and \( R \) are small, and a
phase separated region when attraction is increased at
low \( \phi \). There is a large region (currently explored in ex-
periments [18, 22]) where a homogeneous, equilibrium, transient gel is formed. In the present work we have ex-
plored the interplay between the glass transition at large
vol-
ume fraction and gelation at large \( R \), where we dis-
covered new dynamical phenomena. The iso-relaxation

\[ \Delta^2(t) = \frac{1}{N} \sum_i \langle (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2 \rangle. \]
time lines reported in Fig. 5 obtained for $\tau_{\text{link}} = 1.0$ and defined by $F_s(q, \tau) = 0.03$, show that the dynamics slows down both by increasing $\phi$ or $R$. In the region where both $R$ and $\phi$ act as a source for slow dynamics we generically obtain a three-step relaxation process, which produces for specific combinations of $R$, $\phi$, and $\tau_{\text{link}}$, a logarithmic decay towards 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. 3 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, 12, 23], although of course the relaxation time can get very large if both $R$ and $\tau_{\text{link}}$ 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 timescale [1]. As suggested also from simulations of particles with attractive patches [24], 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 lengthscales and well-separated timescales for cage/bond relaxation. We suggest that the observation of a two-step process for yielding in a sheared colloid-polymer mixture [25] 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 lengthscales, thus opening the door to the creation of new materials.

Financial support from Spanish project FIS2009-08451 and ANR’s TSANET and SYSCOM is acknowledged.

[1] K. Binder and W. Kob, Glassy Materials and Disordered Solids (World Scientific, Singapore, 2005).
[2] A. Imhof and J. 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. E. Stanley, arXiv:0910.3673.
[6] A. M. Puertas and M. Fuchs, in Structure and functional properties of colloidal systems, Ed. R. Hidalgo-Alvarez (Taylor and Francis, London, 2009).
[7] M. Bernabei, A. J. Moreno, and J. Colmenero, Phys. Rev. Lett. 101, 255701 (2008).
[8] D. Bonn, H. Kelguy, G. Wegdam, and J. Meunier, Langmuir 15, 7554 (1999).
[9] T. Eckert and E. Bartsch, Phys. Rev. Lett. 89, 125701 (2002).
[10] K. N. Pham, A. M. Puertas, J. Bergenholtz, S. U. Egelhaaf, A. Moussaid, P. N. Pussey, A. B. Schofield, M. E. Cates, M. Fuchs, and W. C. K. Poon, Science 296, 5565 (2002).
[11] S. H. Chen, W. R. Chen, and F. Mallamace, Science 300, 619 (2003).
[12] 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).
[13] A. M. Puertas, M. Fuchs, and M. E. Cates, Phys. Rev. Lett. 88, 098301 (2002).
[14] F. Sciortino, P. Tartaglia, and E. Zaccarelli, Phys. Rev. Lett. 91, 268301 (2003).
[15] X. H. Lu, S. G. J. Mochrie, S. Narayanan, A. R. Sandy, and M. Sprung, Phys. Rev. Lett. 100, 045701 (2008).
[16] P. L. Geissler and D. R. Reichman, Phys. Rev. E 71, 031206 (2004).
[17] P. I. Hurtado, L. Berthier, and W. Kob, Phys. Rev. Lett. 98, 135503 (2007).
[18] E. Michel, M. Filali, R. Aznar, G. Porte, and J. Appell, Langmuir 16, 8702 (2000).
[19] P. I. Hurtado, P. Chaudhuri, L. Berthier, and W. Kob, AIP Conf. Proc. 1091, 166 (2009).
[20] T. A. Witten, Structured fluids (Oxford University Press, Oxford, 2004).
[21] E. Zaccarelli and W. C. K. Poon, PNAS 106, 15203 (2009).
[22] H. Tabuteau, S. Mora, M. Abkarian, and C. Ligoure, Phys. Rev. Lett. 102, 155501 (2009).
[23] J. Bergenholtz and M. Fuchs, Phys. Rev. E 59, 5706 (1999).
[24] E. Zaccarelli, I. Saika-Voivod, S. V. Buldyrev, A. J. Moreno, P. Tartaglia, and F. Sciortino, J. Chem. Phys. 124, 124908 (2006).
[25] K. N. Pham, G. Petekidis, D. Vlassopoulos, S. U. Egel-
haaf, P. N. Pusey, and W. C. K. Poon, Europhys. Lett. 75, 624 (2006).