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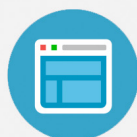Categorization of rheological scaling models for particle gels applied to casein gels
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# Discussion of 019405JOR by R. Zia *et al.*

**Question: Roger Bonnecaze:** From your understanding of the interplay among inter-particle forces, microstructural dynamics, and macroscopic properties of attractive colloidal gels, how would you advise users to formulate the gels to achieve desired properties such as moduli, yield stress, yield strain, and viscosity? In short, how does microscale understanding inform design of these important materials?

**Author Response: Roseanna Zia**: I will focus the response on reversible/weak gels, in contradistinction to strong, fractal gels. The latter undergo little age evolution after network formation, and when formed from dilute dispersions have a fractal structure whose connection to macroscopic properties is well studied elsewhere. The former, weak gels permit a richer range of structure. Our study of the connection between structure and rheology shows that the dominant network length scale sets the magnitude of the visco-elastic response as well as the degree of dominance of the elastic modulus—but individual particle mobility (particle dynamics) also plays a role.

Overall, if one seeks a more elastic than viscous linear response, as long as a space-spanning network has formed, our work shows that the elastic modulus will dominate over all frequencies and ages. If the gel designer seeks to stiffen the linear elastic response, this can be obtained by increasing the dominant structural length scale of the network. Aging a reversible gel with some given attraction strength will lead naturally to coarser structure and hence stronger linear response.

Because a moderate decrease in attraction strength leads to more rapid coarsening, one can achieve higher increases in strength at advanced ages with a slightly hotter gel. The range of validity of this model is approximately $5 \leq U/kT \leq 15$. Beyond this range, users can drastically suppress changes in gel properties with age by increasing attraction strength. However, gel morphology also undergoes qualitative change with large changes in attraction strength. We have not explored the connection between structure and rheology for these stronger gels.

The range of attractions matters, but we have not explored this area thoroughly yet.

Nonlinear responses—yield stress and yield strain—and the connection to structure is an area of vigorous experimental study. We have just begun studies of nonlinear response and will have comments for this question in the coming months. There is a recent work by Petekidis and coworkers suggesting that preshear and/or "rejuvenation" can lead to changes in yield stress magnitude, but the underlying origins of this behavior are not yet fully understood.

**Question: George Petekidis:** Do you think that hydrodynamic interactions would affect not only the microscopic dynamics and time evolution of the gel coarsening (ageing) but also the structure of the metastable gel state at rest or under shear? Computer simulations by Furukawa and Tanaka (2010) suggest that the latter might be possible.

**Author Response: Roseanna Zia**: Yes, hydrodynamic interactions will affect the slow dynamics of gel evolution, but I do not think Furukawa's simple rescaling in time

correctly captures this effect. We are currently studying the effect of pair interactions on quiescent evolution and on response to weak oscillatory shear and will share these results in the coming months.

**Question: George Petekidis:** The interior of the gel strands should be an attractive rather than a repulsive glass. This should be reflected in the dynamics of the participating particles where, for example, the localization length should be much smaller than in a similar volume fraction repulsive glass. Do you have such indications in your simulations? Along this line, is there any indication of logarithmic decays in the intermediate scattering function or the mean square discussion reminiscent of interplay between competing interactions (caging vs attraction), as seen, for example, by Pham *et al.* (2004)?

**Author Response: Roseanna Zia**: Yes, following the results of Pham *et al.* and of Petekidis and coworkers and Laurati *et al.* (2009), we can see that the logarithmic-like relaxation of the SISF bears signatures of an attractive glass. In addition, the faster relaxation of the weaker gel points to the role of attractive forces in glassy dynamics. We have identified the strand interiors as an attractive glass.

**Question: Dimitris Vlassopoulos:** Your work suggests the presence of one dominant length scale in the gel. The work of Colombo and Del Gado (011405JOR) suggests a gradual yielding process, implying multiple length scales. How can we reconcile this? In other words, what is the reason for one length scale in a gel (irrespectively of coarsening or differences in volume fraction/strength of attraction). Or is it system specific?

**Author Response: Roseanna Zia**: The fact that the largest length scale sets the high-frequency behavior can be understood from two perspectives, which we have discussed in detail in the manuscript. First, at high frequency in nonhydrodynamically interacting colloidal *dispersions*, the suspension is perfectly viscoelastic owing to the balance between advection and diffusion inside the boundary layer at contact. Naively, at high frequency the diffusive term can be dropped entirely from an advection-diffusion equation, as diffusion is slow compared to advective oscillation. However, discarding this term results in loss of the no-flux condition at contact; thus the high-frequency perturbation is singular, requiring a thin layer at contact to preserve the no-flux condition. To get an elastically dominated response, one must tip this balance inside the BL and then communicate this disturbance into the far-field. Hydrodynamics can do this. Physically, why does the largest length scale matter? In our work, we claim that the balance is tipped by attractions and then communicated long-range by the network structure. We proposed that the Rouse model is appropriate for modeling relaxation modes in our system (see manuscript for detailed justification.) Asymptotic analysis of the Rouse model—just for its original application to polymer strands—shows that the high-frequency modulus is set by the longest relaxation time scale, corresponding to the longest length scale.

**Question: Najet Mahmoudi:** You showed that there is a time evolution of the dominant correlation length in your arrested phase-separation gels. How do you explain the difference between your results and the experimental results of Conrad *et al.* (2010) on PMMA/PS with a medium range attraction of 0.37, and of Gibaud and Schurtenberger (2009) on lysozyme interacting a short-range attraction, where both showed that the structure of the gels that form via an arrested phase-separation/spinodal decomposition, freezes almost instantaneously; and of Lu *et al.* (2008) who showed that the dominant

correlation length follows a power law of 1/6 during 2 h and then the sample arrests and the dominant correlation length does not change?

**Author Response: Roseanna Zia**: We actually discuss this very contrast in our article. We show that, in contrast to the conclusions of, e.g., Manley *et al.* (2005a), Zaccarelli (2007), and Lu *et al.* (2008), colloidal gels of short-range attraction continue to coarsen long after gelation. In drawing this conclusion, careful attention must be paid to the wavenumber at which peaks occur. Lu *et al.* (2008) have surmised that gels stop evolving at some time after gelation, concluded from apparent cessation in growth of the $S(q)$ peak. However, the wave numbers for the aging gel exist outside the region they studied—that is, at smaller wave numbers $q$. One other possible explanation for the difference between experiment and simulation may be found in the pronounced slowing of coarsening with increasing attraction strength; that is, detection of coarsening may be an issue of temporal, in addition to spatial, resolution. The gels studied by Lu *et al.* reside just inside the gelation boundary, making us suppose these are weak gels; we cannot be certain about this—it may be that their gel was simply stronger than those studied here. For now, we restrict our conclusions to short-range attraction-driven gels.

**Question: Emanuela Del Gado**: Have you tried to characterize particle motion a bit beyond the mean squared displacement, to investigate the presence of correlated and cooperative motion that might bring in further relevant (and possibly larger) length scales into the picture?

**Author Response: Roseanna Zia**: This is an important question. One way to think about this, among others is to study the coherent intermediate scattering function (CISF). Our first pass at analyzing the CISF shows that large-scale, "sudden" cooperative movements do not play a role, i.e., strands do not suddenly coalesce. But the diffusion of the surface particles is most certainly not isotropic, and it is directed in the sense that an underlying driving force leads to their collective motion toward common regions.

**Question: Yogesh Joshi:** 1. Your observation that both $G'$ and $G''$ scale as frequency 0.5 makes you compare the relaxation time distribution with that of Rouse model. However, in Rouse model $G' = G''$ in the limit of high frequency when above mentioned scaling is observed. However, in your simulations $G'$ is always greater than $G''$. How can you therefore justify comparison with Rouse model?

**Author Response: Roseanna Zia**: The Rouse model gives perfectly viscoelastic behavior because it neglects hydrodynamic interactions (see discussion above). The qualitative scaling of both moduli is what sets the Rouse model apart from the Maxwell model, for example, as it accurately predicted this square-root of frequency behavior. Please see discussion above for how we have extended this model into a new model for colloidal gels.

**Question:** 2. It is very interesting to see the presence of glassy domains within the gel. The gels are usually characterized by fractal dimension for length-scales greater than the particle length-scales. Therefore, if aging in gels is causing coarsening to form glassy domains, the local fractal dimension in the same seems to be approaching three in some regions. Should we therefore consider that there is evolution of the fractal dimension at the local level as a gel ages?

**Author Response: Roseanna Zia**: One can measure the trailing edge of the first peak in the static structure factor to gain some idea of fractal dimension. We did so, and in agreement with others (see discussion in our article), we find that $S(q) \sim 1/q^4$ on this trailing edge—consistent with a Porod tail that identifies bicontinuous morphology with clear transition from condensed to dilute phase and smooth surface. That is, the gel is not fractal.

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