

Dear Jim, dear IFPRI members,

Thank you very much for your constructive comments to my proposal in response to your call “Accelerated test methodologies for the physical stability of colloidal dispersions and gels”. I answer to your questions point-by-point below. I hope that you will find my answers convincing and the proposal suitable to your needs.

Yours sincerely,

Luca Cipelletti

Q1. The members are very interested in your optical technique for detecting precursors to gel collapse and believe that for your model system it will provide useful information for understanding mechanisms of gel collapse. There was uncertainty about how well it works for real-life gels, i.e. opaque systems. You say in your proposal that transparency is not required; perhaps you can provide an example of this.

A1. Thank you for your overall positive judgement. The method I propose is based on measurements of the microscopic dynamics using advanced space- and time-resolved dynamic light scattering techniques. The method consists in illuminating the sample with a laser beam and collecting speckle images formed by the light scattered by the sample. The microscopic dynamics between two times t and $t + \tau$ result in fluctuations of the speckle intensity, quantified by the correlator $C_I(\mathbf{r}, t, \tau) \propto \langle I_p(t)I_p(t + \tau) \rangle_r$. $I_p(t)$ is the scattered intensity measured by the p -th pixel of the detector, and $\langle \dots \rangle_r$ an average over a small region of interest (ROI) centered around position r .

To **demonstrate the method on a non-transparent sample**, I have prepared a colloidal gel formed by aggregating commercial Ludox TM50 charge-stabilized colloidal particles (diameter ~ 40 nm), at a volume fraction $\varphi = 1\%$. Aggregation was induced by increasing the ionic strength of the suspension via an enzymatic, *in-situ* reaction. The gel was prepared in a standard glass vial of diameter 2.5 cm and the gel column was about 5.5 cm tall. As shown in Fig. 1a, the gel is opaque, due to strong multiple scattering.

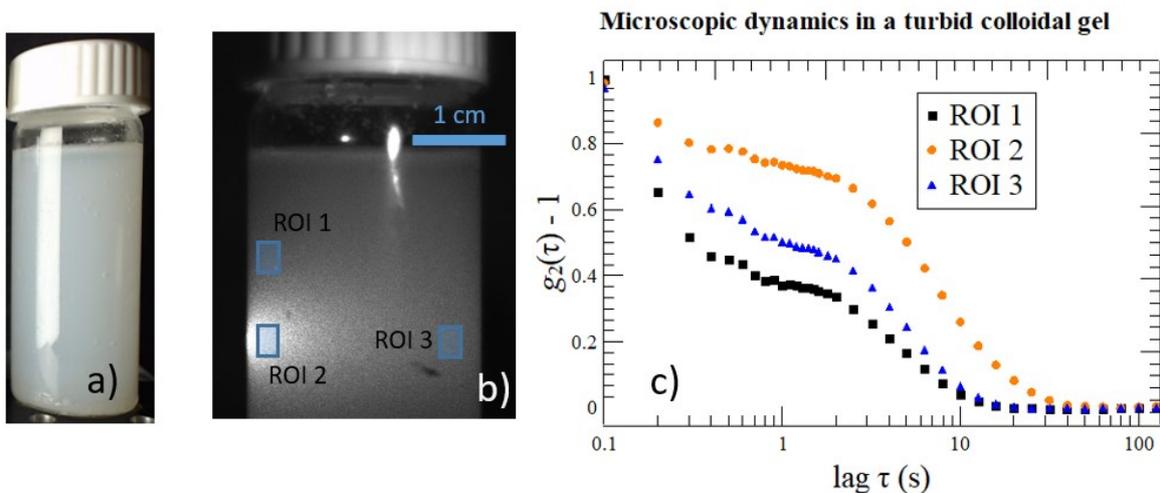


Figure 1: a) image of a turbid gel illuminated by conventional white light. b) Same gel illuminated by a laser beam. The three Regions Of Interest (ROIs) for which the microscopic dynamics were quantified are indicated by the blue rectangles. c) Intensity correlation functions calculated for each ROI, see text for more details.

Figure 1b shows a speckle image collected by illuminating the gel with a laser beam of power 100 mW. The beam had a diameter of about 0.8 mm, it propagated horizontally, and it impinged on the vial just on the left of the Region Of Interest (ROI) labelled ROI 2 in Fig. 1b. Figure 1c shows the correlation functions $g_2(\tau) - 1$ obtained by averaging over time t the correlator C_i introduced above. The following remarks are of interest:

- 1) This simple experiment demonstrates **the feasibility of the kind of measurements I propose, even for turbid samples.**
- 2) The correlation functions exhibit a two-step decay. The initial decay (characteristic time of a fraction of s) is commonly ascribed to thermally activated fluctuations of the gel strands, with no network restructuring. The second decay (time scale of several s), is indicative of network restructuring, potentially leading to weakening of the gel structure. Indeed, the gel did sediment by a few mm in the days following the light scattering measurements (see Fig. 3 below). This preliminary test shows that **the gel restructuring dynamics, which is precisely the quantity we propose to monitor, is accessible by the methods proposed here, even for turbid samples.**
- 3) One can see differences in the g_2-1 functions for the different ROIs. These differences are in part due to the different “mix” of multiple and single scattering according to the distance from the impinging beam. They may also reveal heterogeneities in the gel dynamics, which could unveil localized failure precursors. At this stage, the important point is to emphasize that **space-resolved information can be obtained also for turbid samples.**

Finally, I'd like to emphasize that I have already successfully applied space-resolved light scattering to the investigation of **localized dynamic events in turbid systems**. Two examples are the coarsening dynamics of a foam [D. Sessoms *et al.*, Unexpected Spatial Distribution of Bubble Rearrangements in Coarsening Foams, *Soft Matter* 6, 3030 (2010)] and the instabilities arising during the swelling of a polymer gel [J. Ju, *et al.*, Heterogeneous Nucleation of Creases in Swelling Polymer Gels, *Phys. Rev. E* 105, 034504 (2022)]. I believe that these past works lend further support to the feasibility of the methods proposed here for turbid, real-life gels.

Q2. The most important criticism is that your proposal doesn't address the main objective of the project brief, that of development of accelerated tests for gel stability. This has two components. First, what is the time between the detection of precursors to gel collapse and actual collapse of the gel? Is this long enough to make precursor detection useful compared to more macroscopic analysis, and can the time be predicted from gel properties?

A2. Assessing *a priori* how early a dynamic precursor may precede the macroscopic collapse is a very difficult question. This is precisely **one of the key points that I intend to investigate** in the framework of the present proposal, **as a function of the gel physical and chemical parameters**. Although a quantitative answer cannot be given at this stage, I strongly believe that looking at dynamic precursors is **a very promising way to substantially anticipate the gel collapse**, based on two remarks: 1) macroscopic collapse must result from the accumulation of local damage, via subtle microscopic rearrangements of the network. The technique proposed here can **measure these rearrangements at their very onset**, thanks to its great sensitivity, down to a few nm. 2) We **have already demonstrated dynamic precursors of gel failure in several systems**. One of the most exciting findings concerns agarose gels, for which in [A. Pommella *et al.*, Role of Normal Stress in the Creep Dynamics and Failure of a Biopolymer Gel, *Phys. Rev. Lett.* 125, 268006 (2020)] we coupled rheology measurements to space-resolved dynamic light scattering. We found that samples prepared according to the same protocol

randomly fail (or not) after an induction time of up to tens of hours in creep tests where a constant shear stress was applied. Figure 2a shows a dynamic precursor: a region with faster-than average dynamics is nucleated near the edge of the rheometer tool, at about half the failure time. Even more importantly, gels that did eventually fail had faster microscopic dynamics since the very formation of the gel (Fig. 2b), in spite of all the gels having essentially the same mechanical properties as probed by conventional rheology.

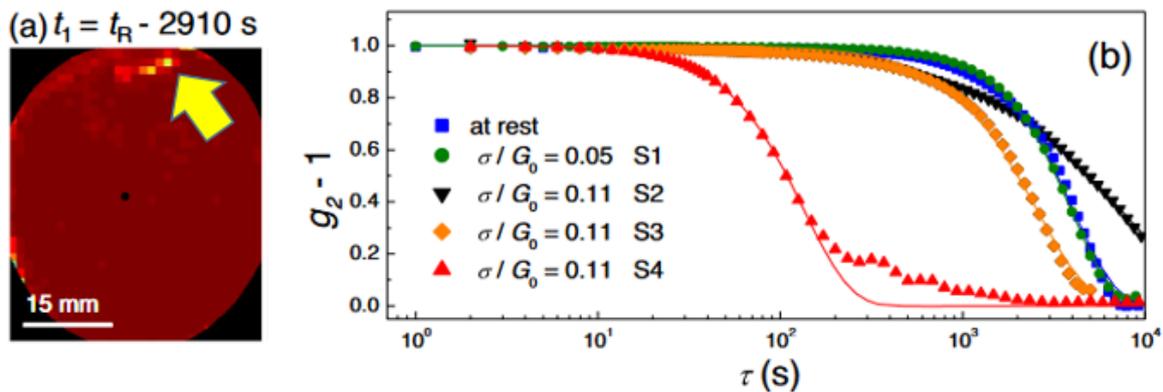


Figure 2 (adapted from A. Pommella *et al.*, Phys. Rev. Lett. 125, 268006 (2020)). a): spatial map of the sample dynamics during a creep test, obtained by dynamic light scattering. The arrow indicates a region near the rim of the plate tool of the rheometer where a dynamic precursor of failure nucleates (bright yellow pixel), which will subsequently expand and invade the full sample. b) Microscopic dynamics measured right after forming the gel and applying a constant shear stress σ (expressed here relatively to the shear modulus G_0), for samples prepared following the same protocol. Sample S4 has much faster dynamics, indicative of a weaker microstructure: it is the only sample that will macroscopically fail.

Q3. Second, how can one deliberately introduce precursors in a reproducible manner and use this to predict the time to gel collapse in industrially relevant situations (e.g. on a shelf or in transport)? Wilson Poon asks if you can take the baseline gel model system you know well and intentionally do things to it known to disrupt it and see if this technique can predict the failure instantly or not.

A3. This is indeed a key point that I did not developed enough in the first submission of the proposal. I propose to spend the first months of the proposal investigating **how the macroscopic collapse time in model gels varies according to gel composition, preparation protocol, and external perturbations**. The goal will be to define a set of “**accelerated aging**” procedures and to test how the microscopic dynamics differ according to the applied procedure.

Accelerated aging may be obtained via a variety of methods, including:

- 1) Varying the gel composition, e.g. increasing the particle radius R or decreasing the volume fraction, or varying the strength of the attractive interactions, or changing the gel-wall interactions. For example, I run a preliminary test that shows that the gel stability depends also on the hydrophobicity of the vessel walls, see Fig. 3. Here, the rationale is **to vary the relative magnitude of the gravitational stress as compared to the yield stress and wall adhesion**.
- 2) Varying the preparation protocol. For example, in preliminary tests on Ludox gels similar to that shown in Fig. 1, we have noticed that the gel stability varies with the way the ionic strength of the initially stable suspension is increased (e.g. by adding salt to the stable suspension and stirring *vs* via an *in-situ* enzymatic reaction, with no stirring). Finally, I propose to vary systematically the temperature at which the gel is prepared, in particular for systems with a DLVO interaction potential, where the role of temperature on the potential is more easily

quantified, as compared to more complex, depletion-based systems. Here, the rationale is **to vary the state of internal stresses and heterogeneities that are inevitably present when an out-of-equilibrium system such a gel is formed**. We expect a more heterogeneous system to be more prone to failure.

- 3) Applying external perturbations to the gel. This may be done mechanically (e.g. with a loudspeaker, or in an ultrasound bath, or with a shaker), or by imposing a thermal perturbation (e.g. a temperature jump, or cyclic T variations). Here, the rationale is **to weaken the gel network in a controllable way, to accelerate its failure**.

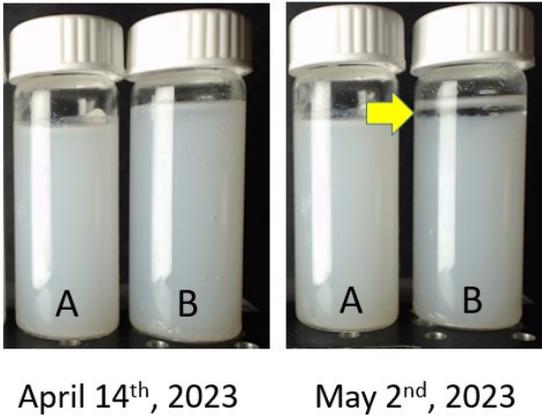


Figure 3. Preliminary stability test on gels formed by Ludox silica particles (same as in Fig. 1). Samples A and B are identical in all respects, except that the walls of vial B have been treated with Sigmacote, a siliconized reagent that makes its surface more hydrophobic. The gel in B started sedimenting after 2 weeks, while the gel in A is pristine.

We plan to investigate systematically the microscopic dynamics of gels prepared or processed/perturbed according to the three points above. The goal will be **to establish correlations between the microscopic dynamics and their variation upon a perturbation and the collapse time**. Some variations may be easy to pick up, e.g. as for the faster dynamics of the gel that eventually fails shown in Fig. 2b. Other correlations may be subtler, e.g. those associated to temporal or spatial fluctuations of the microscopic dynamics. Depending on the background and interests of the postdoc I plan to recruit, machine learning methods may be used to explore these subtler correlations.

Finally, I emphasize that the methods listed here will be enriched and expanded through exchanges and feedback from the IFPRI members, in particular taking advantage of the IFPRI meeting at year 1 of the proposal.

Finally, you asked if dispersion stability is of interest as well as gel collapse. The answer is yes!

Thanks for the answer. As mentioned in the proposal, I propose to develop a new method that combines measurements of the Brownian dynamics (diffusion coefficient D) and of the sedimentation velocity v of colloidal particles in order to assess the stability of a dispersion. I have shown in [L. Cipelletti *et al.*, Simultaneous Measurement of the Microscopic Dynamics and the Mesoscopic Displacement Field in Soft Systems by Speckle Imaging, *Optics Express* 21, 22353 (2013)] that space-resolved dynamic light scattering can measure simultaneously the drift velocity of a suspension (here, due to sedimentation) and its microscopic dynamics (here, due to Brownian diffusion). In particular, I propose to measure the ration between the sedimentation velocity v and the diffusion coefficient D . We expect v/D to scale as R^3 , with R the radius of the colloidal particles or aggregates. Note that v/D varies more steeply with R as compared to v ($v \sim R^2$) or D ($D \sim 1/R$) alone, which will ensure great sensitivity to small changes of R , thereby allowing for early detection of aggregation.