

# IFPRI Proposal: Accelerated test methodologies for the physical stability of colloidal dispersions and gels

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## Abstract

This document presents our response to the IFPRI call for proposals “Accelerated test methodologies for the physical stability of colloidal dispersions and gels”. It addresses mainly the stability of **colloidal gels**, with some possible extensions to dispersions. The proposal addresses in particular the third key element mentioned in the call: the identification of **alternative methods which predict long-term stability of suspensions and gels**. The method we propose is based on non-conventional, advanced light scattering techniques that we have developed in our lab over the years. These methods report with great sensitivity and both spatial and temporal resolution the microscopic dynamics of gels and suspensions. The proposal is based on the idea that **measurements of the microscopic dynamics** with time are a **powerful predictor of the gel collapse**. The proposal thus addresses also the first key point of the call (“Measurement of the local structure with time”), but with a **paradigm shift**, from the local *structure* to the microscopic *dynamics*. We argue that the method proposed here is more easily transferable from model systems to real-life applications, as compared to structural measurements.

## 1. Overview

Colloidal gels formed by “weakly” flocculated particles may suddenly and catastrophically collapse under gravitational stress after an induction time that may last up to days or even months, with little if any precursor signs at the macroscopic level (see e.g. [Royall2021] and references therein). Local rearrangement events that progressively weaken the network must be responsible for this behavior. Indeed, several works have pointed out changes in the local structure with time. In [Poon1999], dark field, low-magnification imaging revealed the formation of “lumps” (local denser regions), followed by vertical “channels” that eventually led to macroscopic solvent transport through the gel and network failure. Using confocal microscopy, [Bartlett2012] showed that the gel coarsens during the induction time. Thanks to an ad-hoc emulsion system comprising a dye sensitive to forces, the authors of [Dong2022] could quantify the force chains within a gel made of emulsion droplets, potentially paving the way to following its time evolution in collapsing gels.

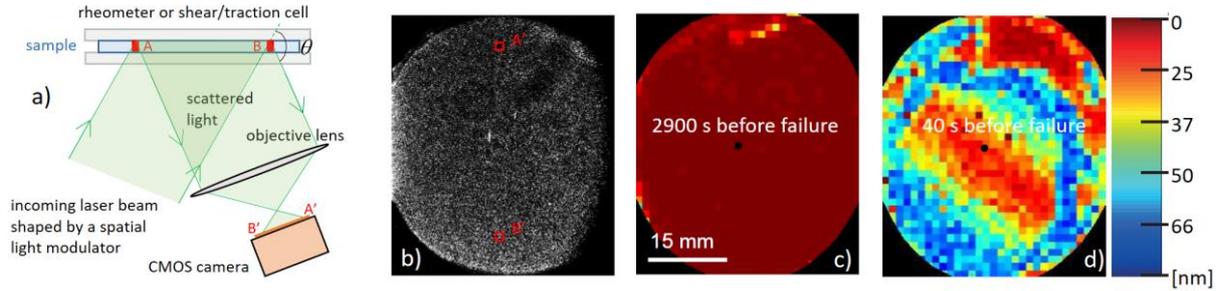
While direct-space imaging methods are very powerful, they suffer from several disadvantages: they typically need ad-hoc systems (e.g. nearly transparent, with fluorescent dyes if confocal microscopy is to be used), they usually probe a small portion of the sample (less than 1 mm<sup>3</sup>), itself part of an overall mm-sized sample chamber, whose size and aspect ratio are very different from those of real-life containers. This latter point is a severe limitation, because the gravitational collapse is known to depend on the size of the container [Royall2021].

To overcome these limitations, we propose to focus on **the time evolution of the microscopic dynamics** as measured by **dynamic light scattering** (DLS) or **diffusing wave spectroscopy** (DWS), rather than the local structure. This is motivated by the following: 1) in amorphous systems, changes in the dynamics are more easily detected than changes in the local structure; 2) we have developed a series of methods combining imaging and DLS/DWS, thereby allowing for the spatial mapping of the

microscopic dynamics [Duri2009]; 3) we and others have recently shown the existence of dynamic precursors of failure, i.e. changes in the dynamics that largely precede the macroscopic failure of soft solids under stress [Cipelletti2020]; 4) the methods proposed here are in principle scalable to real-life samples and do not require the sample to be transparent.

## 2. Space- and time-resolved measurements of the microscopic dynamics

To briefly describe the technique and illustrate how powerful the notion of dynamic precursor may be, we show in Fig. 1 an example for an agarose gel [Pommella2020]. Note that in Fig. 1 the gel is loaded in a rheometer and submitted to a constant shear stress. For studying the gravitational collapse of gels, the apparatus will be modified, as discussed below in Sec. 3, but the overall concept will be similar.



**Figure 1:** space- and time resolved light scattering. a): optical scheme. A, B: distinct sample locations imaged in A', B' in b). For weakly scattering samples, the sensitivity to microscopic motion is set by the scattering angle  $\theta$ , independently of the field of view, which is set by the magnification of the objective lens. For very turbid samples (DWS regime), we will use  $\theta \approx 170^\circ$  and achieve nm-scale sensitivity to microscopic dynamics. b): speckle image recorded for an agarose gel under a constant shear stress. The degree of correlation  $C_I(\mathbf{q}, \mathbf{r}, t, \tau)$  is calculated from a time series of images. It quantifies the dynamics with space and time resolution. Traditional light scattering, by contrast, only provides the average of  $C_I$  over  $t$  and over the whole sample volume. c), d): dynamic activity maps showing the displacement of gel strands over a lag  $\tau = 1$  s, well before and just ahead mechanical failure, respectively.

As shown in Fig. 1a, laser light scattered by the sample forms an image onto a camera detector; due to interference effects, the image has a speckled appearance, Fig. 1b. The microscopic dynamics between times  $t$  and  $t + \tau$  result in fluctuations of the speckle intensity, quantified by the correlator  $C_I(\mathbf{q}, \mathbf{r}, t, \tau) \propto \langle I_p(t)I_p(t + \tau) \rangle_r$ .  $I_p(t)$  is the scattered intensity measured by the  $p$ -th pixel of the detector,  $\langle \dots \rangle_r$  an average over a small region of interest (ROI) centered around position  $\mathbf{r}$ , and  $\mathbf{q}$  the scattering vector associated to the scattering angle  $\theta$  shown in Fig. 1a.  $C_I$  may be converted into a microscopic displacement  $\Delta \mathbf{R}(\mathbf{q}, \mathbf{r}, t, \tau)$  using standard light scattering formalism, or may be just used as is, if comparing the dynamical state at different times and sample locations is sufficient. By repeating the procedure for all ROIs, **dynamic activity maps** are built (Fig. 1c-d).

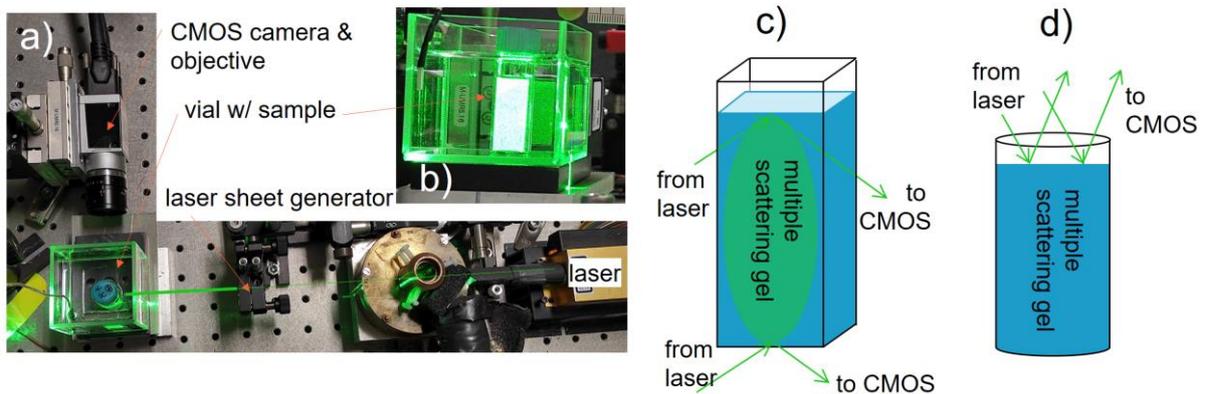
The method combines scattering and imaging. It has **four unique features**: (1) unlike conventional scattering, it is space- and time-resolved; (2) it is sensitive to motion on length scales as small as 1 nm; (3) unlike in conventional imaging, the broadness of the field of view is not limited by the desired sensitivity to motion; (4) the sample constituents do not need to be individually resolved, resulting in general applicability.

As a demonstration of the notion of dynamic precursor of failure, Fig. 1c-d show dynamic activity maps obtained from  $C_I(\mathbf{q}, \mathbf{r}, t, \tau)$  for an agarose gel under a constant shear stress (creep test). Crucially, a region of faster dynamics (top of Fig. 1c), indicative of fast local restructuring, nucleates thousands of seconds before failure and eventually develops in an extended region of intense plastic activity (Fig. 1d) that sweeps across the gel, leading to mechanical failure. Dynamic precursors like those of Fig. 1c emerged roughly at  $t_{\text{fail}}/2$ , with  $t_{\text{fail}}$  the induction time between applying the constant stress and

macroscopic failure. Even more strikingly, in [Pommella2020] we showed that the gel dynamics measured at the very beginning of the experiment could predict the ultimate fate of the gel. Due to the stochasticity of gel formation and rupture, gels prepared with the same protocol would or would not fail over the observation time window (1-2 days). However, gels that eventually did fail exhibited since their formation significantly faster dynamics as compared to gels that did not fail, thus demonstrating the great potentiality of dynamic measurements as a tool to anticipate the gel stability under a mechanical load.

### 3. Apparatus for studying the (delayed) gravitational collapse of gels.

We propose to **build a series of space- and time-resolved light scattering apparatuses** to adapt the concept of Fig. 1 to a suitable geometry. For weakly scattering samples (DLS regime), we propose to use transparent containers (e.g. conventional vials), illuminated by a vertical laser sheet, as shown in Fig. 2a. In this case, the CMOS camera takes images of the sample formed by light scattered at 90 deg with respect to the incident beam direction. Figure 2b shows a vial of height  $\sim 4$  cm containing a gel illuminated by the laser sheet. Figure 2c shows the geometry for a highly scattering, turbid sample (DWS regime) in a transparent container. Here, the image is formed by light backscattered by the sample. Finally, Fig. 2d shows an alternative DWS backscattering geometry, where the sides of the sample container are not necessarily transparent and the incident and backscattered light pass through a transparent cover.



**Figure 2:** space- and time resolved light scattering setups for studying delayed sedimentation of gels. a) and b): setup for weakly scattering gels, illuminated by a laser sheet in the vertical plane. Here, the container is a vial  $\sim 4$  cm tall, but taller containers are possible. Scale: the ruler in the top-right corner of b) is graded in mm. In all cases, the detector takes images of the sample formed by scattered light. As a result, the images have the same speckled appearance as in Fig. 1b and will be processed as described in Sec. 2.

The sample will be immersed in a water bath to reduce refraction effects at the sample/surrounding medium interface and to allow for temperature control (not yet implemented in Fig. 2a,b).

### 4. Outline of the proposed experiments

For **collapsing gels**, we propose to measure the time evolution of the gel height  $h$  (which can be easily obtained from images like that in Fig. 2b) and, in parallel, that of the microscopic dynamics, as quantified by the correlator  $C_l$  introduced in Sec. 2. We will look for dynamic precursors of failure, by investigating quantities such as the dynamics right after gel formation, their temporal evolution, the degree of temporal and/or spatial heterogeneity of the dynamics (e.g. the emergence of “hot spots”

as in Fig. 1c, indicative of significant local rearrangements of the gel structure). Our goal will be to establish correlations between the early stage dynamics and the long term evolution of  $h(t)$ , including the occurrence and time of macroscopic failure.

In addition to exploring the effect of changing the sample parameters (concentration, amount of depletion agent etc.), **we propose to investigate the effect of two other parameters**, which are likely to influence the gel stability: the **boundary conditions** (size and shape of the container, adhesion to the walls) **and fluctuations of temperature**,  $T$ . For the former, depending on the interest by IFPRI, besides changing the shape/size of the container, we will change the wall adhesion conditions, e.g. by coating the walls with suitable polymers, as in [Pommella2020]. Concerning the latter, we will investigate the effect on gel stability of periodic changes of  $T$ , which are likely to occur in real-life storage conditions and may weaken the gel through repeated cycles of expansion/contraction of the solvent.

While our proposal focuses mainly on collapsing gels, an extension of the methods proposed here to the investigation of the **stability of a colloidal dispersion against flocculation** will be pursued, depending on the interest of IFPRI. In general, a non-buoyancy matched colloidal particle of radius  $R$  undergoes Brownian diffusion –with a characteristic time<sup>1</sup> that *increases* proportionally to  $R$ – and sedimentation or creaming, with a time scale that *decreases* as  $1/R^2$ . Light scattering is sensitive to both kinds of motion. The relative importance of either mechanism in determining the overall relaxation time of the correlation functions measured by DLS depends on  $R$  and on the geometry of the experiment (choice of the scattering angle).

We propose to **monitor the time evolution of correlation functions measured by DLS** at a scattering angle where the two contributions are roughly equally important. Because of the strong and opposite dependence of the two contributions on  $R$ , we expect significant changes of the relaxation time and shape of the correlation functions upon the onset of flocculation, due to the increase of the effective hydrodynamic radius of the aggregates that may form. We expect the method proposed here to be much more sensitive than conventional DLS approaches based on measuring Brownian diffusion alone.

## 5. Program for the three years, use of funds

### Year 1:

1.1) Identify good model system for studying gel collapse. We aim at developing a system where delayed sedimentation occurs on a time scale of a few days at most and can be tuned. Furthermore, the gel should be nearly transparent to allow for space-resolved DLS (single scattering conditions). A possible candidate is the system of [Brambilla2011] (nearly index-matched fluorinated particles in a water/urea solution, flocculated by TX100 micelles).

1.2) Adapt existing setups of our lab for space-resolved DLS on collapsing gels. In particular, implement temperature control.

1.3) Explore if the method proposed for the early detection of flocculation of colloidal dispersions is promising, using a model system (e.g. spherical, nearly monodisperse samples).

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<sup>1</sup> The characteristic time is typically defined as the time it takes for the particle to be displaced over a distance equal to its size.

## Year 2:

2.1) Continue the space-resolved DLS experiments of Year 1, exploring the role of sample composition, of the size/shape of the container, of the wall adhesion conditions and of changes (e.g. cycles) of temperature.

2.2) Identify a suitable system for investigating gel collapse under DWS conditions (highly scattering, turbid sample). Test the two DWS geometries (Fig. 2c and 2d) on the same sample.

2.3) Depending on the outcome of 1.3): extend the investigation of the early detection of flocculation to more complex particles, e.g. non-spherical.

## Year 3:

3.1) Collapsing gels: apply the methods developed in years 1 & 2 to more realistic samples and other kinds of gels (e.g. including non-spherical particles, systems based on bio-sourced components etc.). Here, the input of IFPRI members will be crucial in defining or providing test systems as close as possible to real-life ones.

3.2) Depending on the outcome of 1.3) and 2.3), apply to realistic samples (provided or suggested by IFPRI members) the method for the early detection of flocculation proposed above.

Most of the hardware required for the project is already existing in my lab. Accordingly, if IFPRI will sponsor this proposal, I plan to use most of the funding to hire a postdoc, who will conduct the research under my direct supervision. Other funds available in my group will be used to complete the IFPRI funds to pay for a full postdoc salary.

## 6. Relationship with ongoing research programs in our group

I'm currently involved in **several research programs that are related to this proposal**. The continuous development of the light scattering methods proposed here is at the heart of my research since the early 2000's. I've worked on sedimenting gels (see e.g. [Brambilla2011]) and I'm involved in an ESA-sponsored project for probing the dynamics of gels in microgravity conditions (the experiments are planned onboard the International Space Station early 2024).

I'm currently working on the syneresis of polymer gels, using methods similar to those proposed here, including the control of gel adhesion to the walls.

Finally, after studying for many years the spontaneous dynamics of gels and jammed soft matter, since several years I've switched the focus of my research on the relationship between the microscopic dynamics and the macroscopic response of soft solids under a mechanical drive. Overall, there is a **strong overlap between the topic of the IFPRI call for proposal and my current research interests**, which will allow for beneficial cross-breeding between the IFPRI-sponsored activity and my other projects.

## 7. Collaborations

I'm part of a lively soft matter group at University of Montpellier, comprising 16 permanent researchers and several PhD students and postdocs. We have regular discussions about our ongoing projects and a collaborative approach. I plan in particular to collaborate with Laurence Ramos, who is an expert in rheology and in designing soft matter systems, including bio-sourced systems and for applications in the food industry. I also plan to collaborate with Roberto Piazza (Politecnico di Milano, Italy), with whom I have a long-standing collaboration on gels, including in the ESA project mentioned above.

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