



# On line diffusing wave spectroscopy during rheological measurements: A new instrumental setup to measure colloidal instability and structure formation in situ



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## ABSTRACT

A novel setup was employed to investigate the destabilization of colloids, using a rheometer in line with diffusing wave spectroscopy (DWS) in backscattering mode. The newly designed system consists of a concentric cylinder couette geometry fitted with a window to perform simultaneous light scattering measurements. To test the ability of this Rheo-DWS setup to follow the dynamics of destabilization of model systems such as skim milk and emulsions, parallel experiments were also carried out using a separate transmission DWS equipment. For skim milk, containing 10% of volume of protein particles (casein micelles) of about 200 nm in diameter, the physical constraints imposed by the rheological setup did not allow calculation of the correct value of the diffusion coefficient, as the diffusion approximation could not be fulfilled. On the other hand, for concentrated milk (4× the original volume fraction) and for oil in water emulsions, the characteristic decay constant,  $\tau$ , yielded correct size values calculated using known DWS theory. The ability to follow the dynamics of early gelation using Rheo-DWS was tested by measuring the changes occurring during gelation of skim milk, concentrated milk and emulsions. There were no statistically significant differences between the gelation times measured in situ using backscattering DWS and transmission DWS. The data obtained by light scattering were in full agreement with rheology experiments. The results demonstrate the potential of such setup to follow the dynamics of colloidal destabilization and structure formation in situ while subjecting them to simultaneous rheological measurements.

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## 1. Introduction

The observation of the changes occurring in complex fluids, such as colloidal aggregates, surfactant solutions and polymer blends, is of fundamental importance to better understand and control structure-formation in soft materials. In food materials in particular, the changes occurring during colloidal destabilization may lead to important characteristics of the structure of the final matrix—critical to the product's final texture, sensory perception and ultimately consumer acceptance. Traditionally, scattering methods (light, X-ray, neutron) have been used to probe the dynamics of these large-scale structures, as they are optimally suited to obtain insights into the diffusional motion of colloidal constituents (Corredig & Alexander, 2008; Lopez-Rubio & Gilbert, 2009). In particular, diffusing wave spectroscopy (DWS) has been employed to measure sol-gel transitions and colloidal destabilization, as it is possible to follow, in situ, without dilution, the evolution of the turbidity ( $1/l^*$ ) parameter and the diffusivity of the scattering particles (Corredig & Alexander,

2008). Indeed, the  $1/l^*$  parameter is a function of the physical properties of the scattering particles, as well as their spatial correlations, and a change in the diffusion coefficient, derived from the decay time, may be a result of aggregation. Rheological methods are equally suitable for the investigation of colloidal particle destabilization, especially when the changes lead to formation of structures, aggregates, and gels, or when the destabilization is caused by shear. Scattering and rheological methods probe at different length scales, and a simultaneous observation of colloidal destabilization with both techniques is highly desirable to be able to better model processing changes in food matrices.

Several authors have developed theoretical models coupled with novel rheo-light scattering instruments to tackle this question. Original experimental setup of light scattering coupled with rheology has been previously published, for example, to measure light scattering profiles for polymer systems under shear (Ferri, 1997; Lauger & Gronski, 1995; Tromp, Rennie, & Jones, 1995). Systems continue to be developed to follow, in real time, the rheological behavior of complex materials such as bread dough or polymer composites (Arora, Nandi, & Winter, 2011; Fisher & Kroger, 2011). The concept has been extended to other spectroscopic techniques, for example ultrasound spectroscopy, which was employed to investigate the changes under shear flow of hardened red cells in saline solutions (Haider, Snabre, & Boynard, 2004). Though

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the advances made in the field of rheology-light scattering and optical methods have been vast, most literature focused on the instrumental and theoretical development of these techniques. Very few studies have dealt with the application of these methodologies to the investigation of food systems (Van der Linden, Sagis, & Venema, 2003). Light scattering has been previously applied to yield structural information of emulsions during flocculation and sol–gel transitions (Blijdenstein, van der Linden, van Vliet, & van Aken, 2004; Ruis, Venema, & van der Linden, 2008). Recently, a setup with a rheometer and light scattering (Rheo-DWS) was employed to investigate the shear flow behavior of milk as well as the localization of shear planes in stirred yogurt (Raudsepp, Callaghan, & Hemar, 2008; Raudsepp, Feindel, & Hemar, 2010).

The objective of this work was to apply the Rheo-DWS setup to observe the well-known dynamics of structure formation in food colloids, in particular, the progressive gelation of milk during renneting and the isoelectric destabilization of protein stabilized emulsions. Indeed, there are clear advantages to use a Rheo-DWS setup to investigate the destabilization behavior of colloids under realistic conditions, as for example, under shear. However, it is first necessary to determine if the changes occurring to this system, as measured by the dynamic light scattering experiment, are affected by the oscillatory motions induced by the rheometer, and if the physical setup of the rheometer allows for a straight-forward calculation of the light scattering parameters obtained by DWS.

The present work was carried out employing well understood colloidal systems such as skim milk and sodium caseinate stabilized emulsions, undergoing processes also very well described in the literature (Corredig & Alexander, 2008; Sandra, Cooper, Alexander, & Corredig, 2011). Skim milk contains protein particles composed of caseins, dispersed in serum, with an average diameter of about 200 nm (Dalglish, 2011). These aggregates are sterically and electrostatically stabilized by  $\kappa$ -casein, a “hairy” layer protruding from the surface of the micelle and into solution (Dalglish, 2011; De Kruif, Huppertz, Urban, & Petukhov, 2012). Addition of the specific enzyme chymosin (rennet) is the basis of the formation of milk gels and causes the breakdown of the  $\kappa$ -casein and the subsequent aggregation of the casein micelles (de Kruif & Zhulina, 1996). The second model system subject of this study is a sodium caseinate stabilized soy oil emulsion. Sodium caseinate is widely used as an emulsifier in food products, as it provides long-term stability of oil droplets against aggregation through a combination of electrostatic and steric stabilization (Dickinson, 1999). At high pH and above its isoelectric point, caseinate-coated droplets are negatively charged, but a reduction of the surface charge during acidification causes a decrease of the thickness of the double layer with eventual destabilization of the oil droplets (Chen & Dickinson, 2000; Dickinson, 2010).

The main objective of this work was to determine if the geometric constraints imposed by rheology affect the ability to interpret the light scattering data in dairy-based system. In addition, the study determined if oscillatory measurements can be performed during sol-transitions of these colloidal systems without disturbance to the light scattering signal. The results derived from this research will extend the potential utilization of the Rheo-DWS technique to study simultaneously the destabilization of food colloids using two complementary techniques.

## 2. Materials and methods

### 2.1. Sample preparation

Fresh milk was collected from the Ponsonby Research Station of the University of Guelph (Guelph, Ontario). After addition of sodium azide (0.02% w/v) (Fisher Scientific, Mississauga, Canada), milk was skimmed at 6000 g for 20 min at 4 °C (Beckman–Coulter centrifuge, model J2-21, Beckman Coulter, Mississauga, Ont., Canada) and filtered through glass microfibre filters (Whatman Inc., Florham Park, USA) as previously described in detail (Sandra et al., 2011). Skim milk was concentrated

by ultrafiltration at room temperature using a regenerated cellulose filter with a 10 kDa Nominal Weight cutoff (Millipore Corporation, Bedford, MA, USA). The concentration factor was determined by the volume of permeate removed. For the 4× concentrated skim milk, 225 ml of permeate was removed from a volume of 300 ml of milk.

Sodium caseinate stabilized emulsions were prepared by dispersing 0.55% (w/v) sodium caseinate (NaCas) (New Zealand Milk Proteins, Mississauga, Ontario) into MilliQ water. This solution was kept at room temperature and under continuous stirring for at least 1 h.

The oil-in-water emulsions were prepared by adding 10 ml of soybean oil (Sigma Aldrich, St. Louis, MO) into 90 ml of the protein solution, for a final emulsion of 10% (v/v). The samples were premixed for 1 min using a high-speed blender (PowerGen 125, Fisher Scientific, Co., Nepean, ON) and finally passed through a laboratory scale, high-pressure homogenizer (EmulsiFlex C5, Avestin, Ottawa, ON) with three passes at 40 MPa.

### 2.2. Gelation

Skim milk was destabilized using rennet enzyme. Gelation was induced using CHY-MAX® ULTRA rennet (CHR-Hansen, Milwaukee, USA) with 790 IMCU/ml (double strength). For each experiment the rennet dilution was freshly made and added to 30 ml of skim milk at 30 °C and mixed thoroughly for 20 s to a final concentration of 0.018 IMCU/ml. More details can be found elsewhere (Sandra et al., 2011).

In the emulsion case, the destabilization occurred by acidification. Glucono- $\delta$ -lactone (GDL) (Sigma Chemical Co, St Louis, USA) was added to the emulsion at a concentration of 0.3% (w/v) and stirred (30 s) at 25 °C. More experimental details can be found elsewhere (Liu, Corredig, & Alexander, 2007). In a parallel experiment, the emulsion was placed in a water bath at 25 °C and the pH was measured with pH-meter AR15 (Fisher Scientific Co., Singapore).

### 2.3. Rheo-DWS measurements

The Rheo-DWS experiment was carried out in backscattering mode. The instrument was built in the laboratory and attached to a commercial rheometer (see below). An extended, vertically-polarized beam from a HeNe laser (wavelength 632.5 nm, power 150 mW, model LHPR 1201 Research Electrooptics, Boulder, CO) was expanded by a beam expander to a diameter of about 2 mm. For details see Fig. 1A. The beam then impinged on the side of the concentric cylinder geometry (bob-and-cup couette) of the rheometer, which was made of glass encased in an outer, stainless steel cylinder donned with an opening to allow the laser beam through (Fig. 1B). This stainless steel jacket was hollow and connected to an external water bath (Isotemp 3016, Fisher Scientific, Whitby, Canada), which pumped water through it, enabling precise temperature control of the sample, which was kept at 30 °C. The bob was made of black PVC to minimize light reflections. The backscattered light collection setup was similar to that explained for transmission measurements (see below), using a single fiber optic bifurcated and fed into two matched photomultipliers (HC120-03, Hamamatsu, Loveland, OH). A correlator (FLEX2K-12 × 2 correlator, Bridgewater, NJ) was used to analyze the data. In the backscattering apparatus, only the perpendicular component was detected (V-H mode).

A controlled-stress rheometer (Paar Physica, Austria) was used for the rheological measurements. The sample (8 ml) was incubated at 30 °C in the purposely-built concentric cylinder geometry (1 mm fixed gap) (see Fig. 1). A time sweep was run at 0.01 controlled strain, 1.0 Hz frequency. The sol–gel transition was defined as the time at which the values of  $G'$  (storage modulus) and  $G''$  (loss modulus) were equal.

### 2.4. Transmission DWS

In addition to Rheo-DWS experiments, transmission DWS experiments were also carried out in parallel, with a separate experimental

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