

## Nonlinear Viscoelastic Properties Measurements in Complex Fluids using Dynamic Acoustoelastic Testing

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### Abstract

Non-contact acoustic methods appear to be an interesting alternative to conventional rheometry, particularly for the characterization of complex systems. A nonlinear acoustic approach, the Dynamic AcoustoElastic Testing (DAET) has been used to measure the nonlinear viscoelastic parameters. In this wave-interaction method, ultrasound pulses probe the sample, and simultaneously a low-frequency sinusoidal acoustic wave (4kHz) compresses and expands the medium, acting as a bulk stress.

In this work, granular media (packed dry PMMA powder, unconsolidated water-saturated and gelatin-saturated glass beads) have been investigated, as well as the creaming effect of hollow beads in water. The granular media have shown a hysteresis and a high value of the nonlinear parameter B/A in case of beads-contact. An additional compression/expansion asymmetry was observed in the hollow beads. Finally, the method allows us to follow a creaming kinetic.

**Keywords:** acoustic rheology, viscoelasticity, non-contact method, nonlinearity, granular

## 1. Introduction

For most products manufacturing, physical properties such as viscoelastic coefficients, are key-parameters for the process optimisation. In addition, the contact-free and non-destructive monitoring of such parameters is of great interest to guarantee, on line, the products compliance to specifications, and its integrity during the manufacturing process. A change in bulk viscoelastic properties is indeed a good indicator of the material quality and performance degradation.

Two different dynamic stresses may be applied to assess viscoelastic properties: shear and normal stresses. Shear viscoelastic properties (complex shear modulus  $G^*$ ), are mainly measured by conventional rheometers [1] or Dynamic Mechanical Analyzers, DMA [2]. Uniaxial or triaxial normal stress allows measuring the bulk viscoelastic properties, such as the Young's or longitudinal modulus, depending on the technique. DMA devices are able to apply bending, tensile or compressive testing thanks to different sample clamps [1, 2]. Tensile testing is also realized by extensional rheology, such as: RME rheometer [3, 4], Filament Stretching Rheometer [5] or opposed jet devices.

Marginally, acoustic techniques have been developed using either shear or longitudinal wave's spectroscopy [6]. These approaches are mainly based on the linear measurement of the wave celerity and attenuation during a frequency sweep [6-9]. However the shear waves are particularly limited by a low shear penetration depth, as explained in [10].

Finally, a different acoustic approach, the Dynamic Acousto-Elastic Testing (DAET), has been developed in our laboratory to assess nonlinear viscoelastic properties [11]. Initially used for micro-cracks detection in bones [12], DAET is well-adapted to microdamage detection in general, but also to the characterization of complex media. The non-contact DAET method appears to be an interesting alternative to investigate the nonlinear viscoelastic properties of complex and fragile systems such as granular media [13], foams or solids.

In this study, we evaluate the sensitivity of DAET approach for the characterization of different complex media. Three granular media (packed dry PMMA powder, unconsolidated water-saturated and gelatin-saturated glass beads) are investigated as well as the creaming effect of hollow beads in water.

## 2. Dynamic Acousto-Elastic Testing (DAET)

### 2.1 Experimental setup

The DAET method is based on the interaction of two acoustic waves: 1. A low-frequency (LF, 4 kHz) sinusoidal wave acting as a bulk compression/dilatation stress on the sample, also called hydrostatic pressure; simultaneously 2. High-frequency (HF) ultrasound pulses probing the sample. The sample consists of a 13mL watertight PMMA container filled with the fluid-medium to be tested. The HF and BF waves are directly generated in the water tank (Figure 1.a). The LF pressure, measured by the hydrophone is considered stable over time (quasi-static) and spatially homogeneous. More details on the method are available in previous papers [11, 14].

The LF wave modulates the HF ultrasound pulses time of flight (TOF). These time of flight modulations (TOFM) are plotted as a function of the LF pressure amplitudes which provide a nonlinear rheological diagram, called “instantaneous diagram” (Figure 1.b).

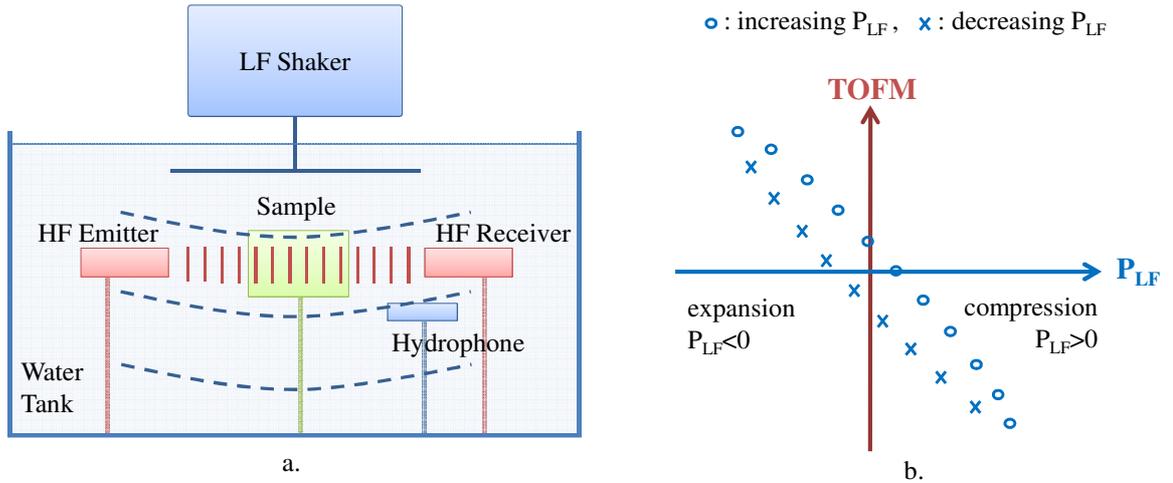


Figure 1 a. Diagram of the experimental configuration, b. Representation of the instantaneous diagram

### 2.2 Assessment of nonlinear viscoelastic properties

TOFM is obtained by a cross-correlation technique between each HF pulse and the reference pulse, which has not been submitted to the LF hydrostatic pressure:

$$TOFM = TOF - TOF_0 \quad (1)$$

The propagation of the HF pulses (quasi plane waves) is governed by the viscoelastic longitudinal modulus  $M$ . Differentiating the relations  $M = \rho c^2$  and  $c = L/TOF$  with  $L$  the distance between the HF transducers,  $\rho$  the density and  $c$  the fluid celerity, and assuming that the variations of  $\rho$  and  $L$  are negligible, TOFM can be directly related to the variations of  $M$  ( $\Delta M$ ):

$$TOFM = -\frac{L}{2\rho_0 c_0^3} \Delta M \quad (2)$$

where the subscript 0 refers to the HF parameters in absence of LF pressure. The first nonlinear elastic coefficient B/A, also called classical nonlinear quadratic parameter [15], can be written as follows [11]:

$$\frac{B}{A} = -\frac{2\rho_0 c_0^3}{L} \left( \frac{TOFM}{\Delta p} \right) \quad (3)$$

The B/A value is obtained from the slope of the TOFM as a function of the LF pressure amplitude (Figure 2.a, red line on the instantaneous diagram). More precisely, this parameter is associated to the elastic component (real part) of the first nonlinear coefficient of the complex viscoelastic modulus. The presence of a hysteresis characterizes a phase delay between the TOFM curve and the applied pressure stress, and it is related to the nonlinear viscous contribution (imaginary part) [16].

DAET measurements performed in water exhibited a linear behaviour between TOFM and applied pressure amplitudes (weakly nonlinear medium without nonlinear viscous contribution), and have provided the expected B/A value of 5 [11, 15] (Figure 2.a).

### 2.3 Preparation of samples

It is not possible for DAET measurement to just and simply fill the PMMA container with the different media to test. The presence of micro-bubbles is indeed an important source of acoustic nonlinearities which modify drastically the results obtained. The different media are hence firstly centrifuged or degassed in a vacuum chamber to get rid of bubbles. The temperature during experimentations is kept constant at 25°C.

In order to validate the DAET method, homogeneous fluids have been tested [17]: tap water, Silicone oil (1000mPa.s dynamic viscosity, Brookfield Engineering Laboratories) and gelatin gel with a weight concentration of 4% (Type A from porcine skin, G2500 Sigma Aldrich).

Different granular samples saturated either with water or gelatin have then been prepared, in order to test more and more complex granular systems:

1. Glass beads (250µm mean diameter, Mineralox) water and gelatin saturated. The beads were randomly distributed in the container. Two solid volume fractions  $\phi$ , defined as the volume occupied by the grains divided by the total volume, have been prepared: 56% and 51%. In the case of 51% an actual free-space exists between beads, leading to an important decrease in the beads contact.
2. Smaller granular materials have also been considered: air-saturated PMMA beads (8µm mean diameter, Ganzpearl). The medium was packed until  $\phi = 60\%$ .
3. Watertight hollow beads filled with air (mean diameter of 16µm) have been placed in the container saturated with water. This floating granular medium therefore presented a creaming phenomenon in time that could be observed.

### 3. Results and discussion

#### 3.1 Results in homogeneous fluids

The instantaneous diagrams in homogeneous fluids (gelatin and silicon oil) exhibited a linear dependence between the TOFM and the low frequency pressure, as it was already observed in water. This result was expected in such homogeneous and monophasic fluids, characteristic of weak elastic nonlinearities (classical quadratic nonlinearity). However a small hysteresis was sometimes observed in silicone oils as seen in Figure 2. As mentioned before, this hysteresis is characteristic of a nonlinear viscoelastic behavior, *i.e.* including an imaginary component in the nonlinear viscoelastic coefficient.

The nonlinear parameter  $B/A$  is calculated for each fluid thanks to the Equation (3). In such homogeneous media, the  $B/A$  values are lower than 15 (weak nonlinearity). Experiments in Castor oils and viscoelastic gels (carbomers and xanthan gums) of different mass fraction in polymer have also exhibited the same “linear” behavior [17].

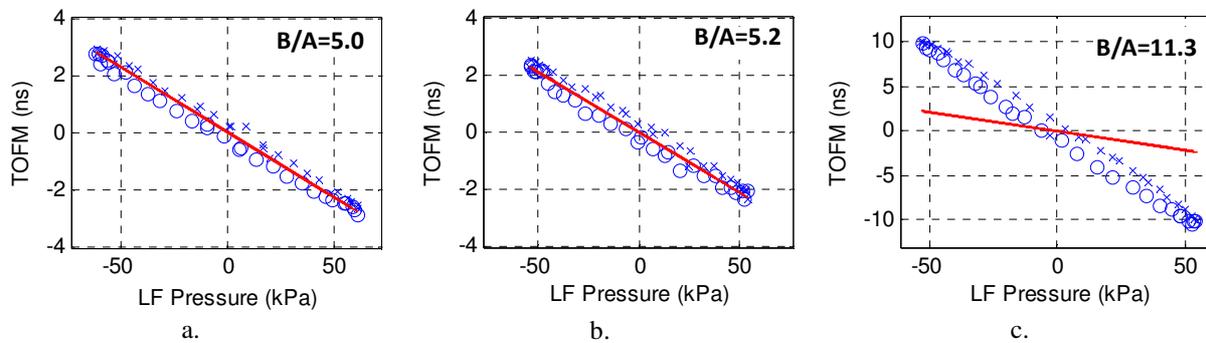


Figure 2. Instantaneous diagrams of TOFM *versus* LF pressure for: a. Water, b. Gelatin gel, c. Silicone oil. The red straight line corresponds to the theoretical curve in water, the cross mark to a value at increasing LF pressure, and the circle mark to one at decreasing LF pressure.

#### 3.2 Results in granular media with large particles

##### 3.2.1 Influence of the surrounding fluid

DAET measurements were performed in 250 $\mu$ m glass beads saturated with water and with solid gelatin. The results are presented in Figure 3.a and Figure 3.b, for the water-saturated sample and gelatin-saturated sample, respectively. The  $B/A$  values kept quite similar (66 and 69), but much higher than in homogeneous fluids.

A hysteresis is also observed in both cases. The presence of solid gelatin slightly decreases the hysteresis. The absolute TOFM amplitude is kept nearly constant,  $\pm 4$ ns, however an important offset is observed in the instantaneous diagrams. These only positive TOFM amplitudes are related to smaller propagation velocity and consequently to a softening of the gelatin-saturated granular medium phenomenon under stress (Equation (2)). This behavior is probably similar to slow-dynamics effect well-known in nonlinear acoustics [18].

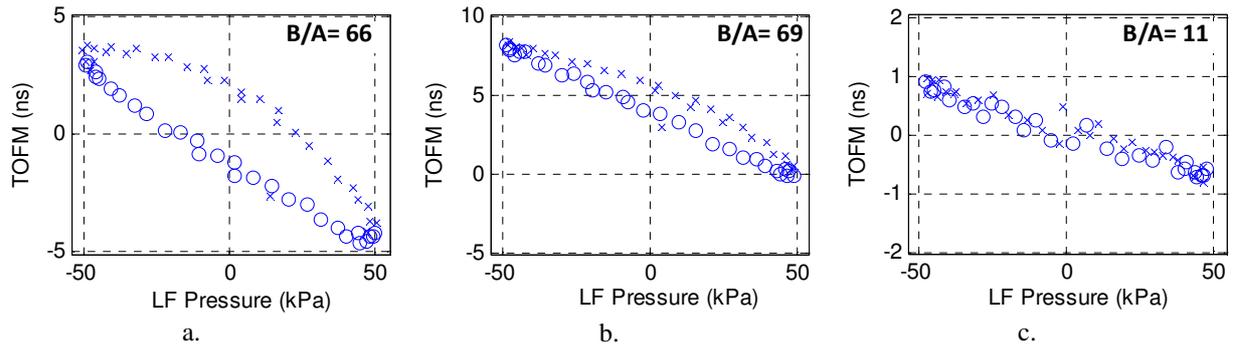


Figure 3. Instantaneous diagrams of TOFM *versus* LF pressure for: a. Glass beads in water ( $\phi = 56\%$ ), b. Glass beads in gelatin ( $\phi = 56\%$ ), c. Glass beads in gelatin ( $\phi = 51\%$ )

### 3.2.2 Influence of the solid volume fraction $\phi$

The results corresponding to an additional gelatin-saturated glass beads experiment with a smaller solid volume fraction of 51% are presented in Figure 3.c. The level of nonlinearity is drastically decreased compared with the 56% solid volume fraction (Figure 3.b): decrease in the B/A value, no more hysteresis, nor offset. The  $\phi = 51\%$  instantaneous diagram is similar to the gelatin-only diagram (Figure 2.b). A rapid microscopy analysis (not presented here) shows that the compacted 56% solid volume fraction presented much more beads contacts than the  $\phi = 51\%$  case. In this latter case, as mentioned before, this gelatin-sample presents an important decrease in the beads contacts. Since the nonlinearities are essentially created by the beads clapping [19] under LF pressure, TOFM amplitudes are obviously decreased. Both viscous and elastic nonlinearities are greatly impacted by the presence of contacts between beads.

### 3.2.3 Influence of the maximal $P_{LF}$ amplitude

When the maximum low-frequency pressure amplitude is regularly increased in the  $\phi = 56\%$  gelatin-saturated glass beads sample, we clearly show that the TOFM curves “nonlinearly” increase (Figure 4.a). In the  $\phi = 51\%$  granular medium, only a scaling factor is observed, as shown in the Figure 4.b.

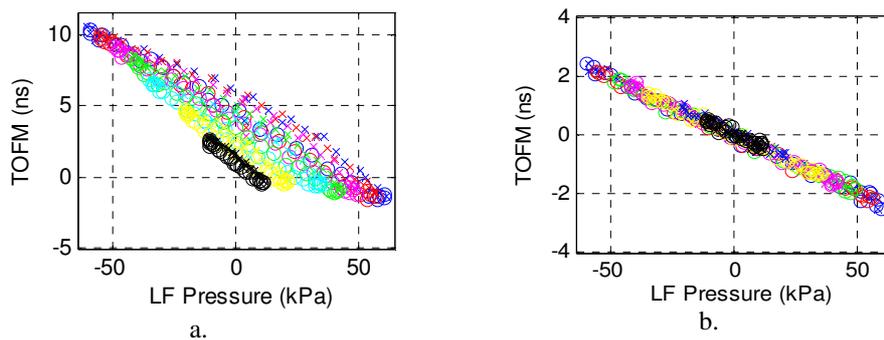


Figure 4. Instantaneous diagrams at different maximal LF pressure amplitudes for: a. Glass beads in gelatin ( $\phi = 56\%$ , full beads contacts), b. Glass beads in gelatine ( $\phi = 51\%$ )

In conclusion, the beads contacts increase the nonlinear behavior: B/A value, hysteresis and offset clearly increase with the maximal LF pressure amplitude applied. Only a small decrease in the beads packing, drastically reduce the level of nonlinearities: same B/A values, no hysteresis, no offset when the maximal LF pressure amplitude is increased. The DAET

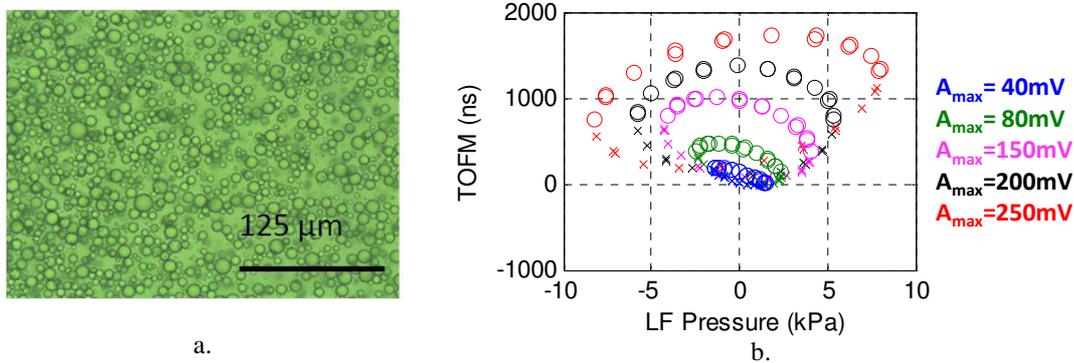
method seems particularly sensitive to the number of beads contacts, and also probably to a threshold effect.

### 3.3 Preliminary results in dry fine powder

We perform DAET experiments in  $8\mu\text{m}$  PMMA beads saturated with air (Figure 5.a). An important hysteresis and a positive offset were observed (Figure 5.b). As mentioned before, it corresponds to a medium softening effect under stress, only appearing in very nonlinear media.

When the maximal amplitude of the LF pressure is increased, the TOFM curves increase “nonlinearly” as seen previously in gelatin-saturated glass beads on Figure 4.a. Furthermore, the B/A value decreases from positive 75 to negative -48, leading to a slope inversion of the instantaneous diagram on Figure 5.b. Here again, this evolution of the B/A parameter proved the highly dependence of the nonlinearity upon hydrostatic pressure.

We have no explanation of this phenomenon today. The HF measurements in this dry powder were quite difficult, since it is very attenuating, and we had to drastically decrease the HF to 70 kHz. The presence of air in the sample also impacts the LF pressure amplitude, which could hardly reach 10kPa. Even with these apparently small LF pressure amplitudes important levels of nonlinearities were measured with the DAET method. The HF pulses propagation velocity is very low in those air-dry granular media, typically 200 to 300 m/s. As expected from equation (3), the TOFM amplitude is particularly high in low celerity medium, even if this medium is weakly nonlinear.



a. Image of PMMA beads with a mean diameter of  $8\mu\text{m}$ ,  
b. Instantaneous diagrams for PMMA beads ( $\phi = 60\%$ ) at different maximal amplitude of the LF pressure. The B/A values are: 75 at 2 kPa, and -48 at 8kPa.

### 3.4 Beads Creaming kinetics

An air-based sample prepared with watertight hollow beads filled with air and saturated in water, has been tested with DAET method and rapidly analysed in microscopy as seen in (Figure 6.a). On this picture we clearly see the solid silicate shell of these beads, and we can also observe an important beads size distribution. The instantaneous diagram (Figure 6.b) presents a strong asymmetry between the compression and expansion phases, a hysteresis essentially in compression and an important negative offset. In phospholipidic ultrasound contrast agents (UCAs), which are also triphasic media, we usually observe a more important nonlinear behavior in compression [20, 21]. However, Marmottant *et al.* have shown that when the shell becomes thicker and more rigid the UCAs resist and can exhibit important levels of nonlinearity either in compression or in expansion [22].

The B/A values are highly negative: -16 at the beginning of the experiment and increases up to -255 seven days later (Figure 6.b). The hollow air-filled beads, which are less dense than the surrounding water, rose up over these seven days. This creaming effect compacts more and more the granular medium, leading to increased nonlinearity amplitudes.

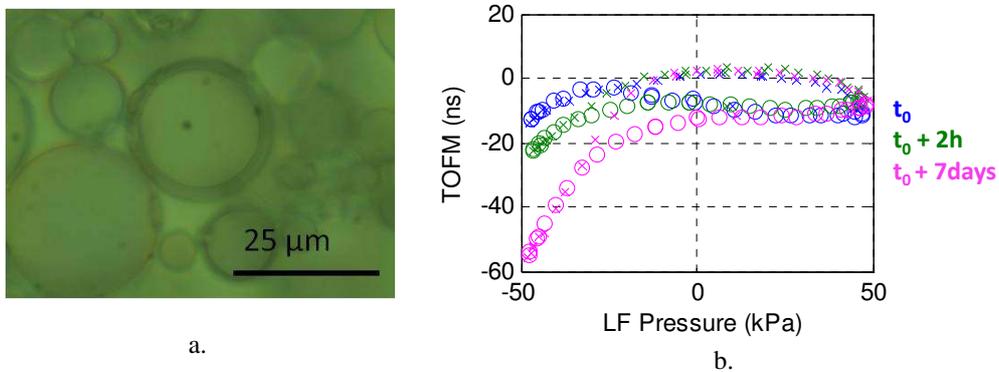


Figure 6 a. Image of hollow beads with a mean diameter of 16μm,  
 b. Instantaneous diagrams for hollow beads at different time. The B/A values are:  
 -16 at  $t_0$ , -94 at  $t_0+2$  hours and -255 at  $t_0+7$  days

## 4. Conclusions

The nonlinear elastic (B/A parameter, offset) and viscous (hysteresis) behaviors of different granular media have been investigated using the DAET method. The viscoelastic nonlinearities are found to be much higher in granular media and hollow beads than in homogeneous fluids. In addition, the level of nonlinearity is highly correlated to the beads contacts, their nature (presence of water or gel), and the LF pressure amplitude. The high sensitivity of the DAET method to the number of contacts between beads (close solid volumes fraction) could be an interesting way to study percolation thresholds in granular media. The DAET method also shows a good performance to follow a creaming kinetic in a granular medium. Similarly, the sedimentation process and also the powder compaction problematic could be interesting applications of this approach.

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