Phase Transition Evaluation of a Medium Using Acoustic Reverberation Time

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Abstract. Non-destructive monitoring of a material’s state during its physico-chemical transformation is of interest for several industrial fields including food processing and industrial manufacturing. Recent research trends have focused on the monitoring of elastic properties (Young's modulus, shear modulus) of sol-gel products. The use of ultrasound to provide reliable information about physico-chemical properties is becoming increasingly popular. In fact, ultrasonic techniques have the main advantage of being rapid and non-invasive methods that allow parameters such as product composition, structure and physical state to be obtained. Yet, classical techniques are limited to the characterization of the medium along the propagation path using first wave packets. In this paper, an alternative technique based on studying the reverberated signals is used, by analogy with those classically used in room acoustics. These complex signals contain useful quantitative and qualitative information about medium properties and are sensitive to structural changes. In previous works, this method has shown its capability to characterize materials. Compared to classical techniques, it has the advantage of studying a medium as its whole structure. Using this method, the determination of sol-gel phase transition of Salol is presented. Measurements were performed using an aluminum mould and nine piezoelectric (PZT) patches randomly distributed on the mould rear face. One of them is used as a source and the others are connected to an eight-channel oscilloscope and are used as receivers. The mean reverberation time over four receivers has been studied and its evolution can be linked to a sol-gel phase transition.

1. Introduction
The term ”sol-gel” was coined in the late 1800s. In contrast with high-temperature processes, the sol-gel technique refers to a low-temperature method using chemical precursors that can produce ceramics and glass with higher purity and better homogeneity. Currently, this process is used in order to produce a large range of compositions in various forms like fibers [1], monoliths [2], composites [3, 4], powders [5], porous membranes [6, 7] and organic/inorganic hybrids [8]. Sol-gel derived products have been used in several fields and industries [9, 10], such as in electronic [11], optical [12], dental [13], bio-medical [14], food processing [15], cosmetic [16], etc. Recent research trends have been focused on the monitoring of elastic properties (Young’s modulus, shear modulus) of sol-gel products [17, 18, 19]. In-situ and non-destructive monitoring of a material state during its transformation (phase transition) is challenging for industrial applications, especially in food (like cheese and other milk derived products) and cosmetics.

Ultrasonic techniques are becoming increasingly popular for providing information about the physico-chemical properties, such as product composition, structure and physical state [20, 21].
These techniques can also be used for continuous monitoring of product properties directly on production lines. Most of classical ultrasonic NDT techniques are based on the study of only the first received wave packets [22, 23], without using the signal coda. They are commonly used to determine the phase change time and the viscosity of a local studied medium. In this paper, a complementary technique based on the study of the reverberated signal in order to estimate the phase transition of a whole structure is proposed.

In case of a high number of propagation paths, wave physics problems can judiciously be treated as a random process. Such approaches are well known for example in multiple scattering [24, 25] or reverberation [26, 27, 28]. These multi-path propagation in whole structure with low acoustic attenuation could offer potentially useful global and local information about the structural properties of this medium using only few sensors [29, 30, 31]. Arguably the most common application of ensemble averaging of reverberated acoustic signals is developed in the field of room acoustics. Thus, the reverberation time (RT) can be easily estimated from Schroeder’s backward integration [32, 33] or envelope averaging technique [34]. Then, the sound absorption coefficients of walls can be estimated using either Sabine’s or Eyring’s law, or a generalised version of these [35]. This well-known example shows that average features on apparently random signals may give access to some useful characteristic properties of the medium.

In this paper, the relation between RT variation and the sol-gel phase transition is presented. This method was inspired from room acoustics techniques and adapted for an aluminum mould. Then, a theoretical relationship is derived from Sabine’s law in order to establish a relation between the RT and absorption coefficient of the interface between aluminum and sol-gel. Subsequently, RT is estimated through a log-linear curve fitting of Schroeder’s integrals, averaged over the several sensors. Finally, an experimental setup has been established in order to validate the principle and to show the feasibility of observing phase transition.

2. Method

Most of the research in acoustic rooms are based on the RT determination, which was introduced in the early twentieth century by W.C. Sabine [36]. In this method, a high modal density allows uniform distribution of sound energy (diffuse field) in the room. During its propagation, the acoustic wave decays due to the fluid attenuation factor Γ and can be described by $E_0 e^{-\Gamma c r t}$, where $E_0$ is the initial energy, $c_r$ is the wave velocity in the fluid and $t$ is the propagation time. When a reflection on a wall occurs, a part of this energy is reflected whereas the other part is transmitted. These phenomena can be modeled as a discrete attenuation $(1 - \alpha)$, where $\alpha$ is the wall absorption coefficient. Therefore the energy over the time in a finite fluid cavity can be written as [37]:

$$E(t) = E_0 e^{-\Gamma c_r t} (1 - \alpha)^{t/t_a}, \quad (1)$$

with $t_a$ the average period of time between two successive reflections, given by

$$t_a = 4V_r/c_r S, \quad (2)$$

where $V_r$ is the room volume and $S$ is the walls total area. Then, the reverberation time needed for the level to decrease by 60 dB ($I_0/I = 10^6$) in air, is given by

$$RT_{-60\,\text{dB}} = 0.16 \frac{V_r}{4\Gamma V_r - S \ln(1 - \alpha)}. \quad (3)$$

Since $\alpha \ll 1$ and assuming that $\Gamma$ is negligible, the equation (3) can be written as

$$RT_{-60\,\text{dB}} = 0.16 \frac{V_r}{S \alpha}, \quad (4)$$
where the constant $0.16$ depends on wave velocity in room fluid ($c_r = 340 \text{ m/s}$) and for an attenuation coefficient of 60 dB. In this paper, empirical Sabine’s equation (equation 4) is adapted in order to study phase transition in a sol-gel. By applying room acoustics technique to a solid medium, we consider aluminum mould equivalent to "room", where reverberation occurs, and the sol-gel equivalent to the walls, where discrete attenuation occurs. Figure 1 shows a typical example of an aluminum mould used in this study. The sol-gel volume is very low compared with that of the mould and assumed to be negligible. By analogy, the volume of mould ($V_m$) is equivalent to Sabine’s $V_r$ and Sabine’s product $S\alpha$ is equivalent to the absorption coefficient $A_m$ (dB.m$^2$) between aluminum mould and sol-gel interface.

\[ RT_{-10\text{dB}} = 0.00145 \frac{V_m}{A_m}. \]

As previously explained, Sabine’s law takes the hypothesis that the intrinsic attenuation of the reverberating medium ($\Gamma$) is negligible and that the attenuation coefficient $\alpha$ is small. In case of Aluminum, the criterion on $\Gamma$ is realistic for this range of frequency ($\Gamma = 0.066 \text{Np/m}$ [31] and $\alpha$ varies from $10^{-4}$ (Air) up to 0.19 for solid salol [38]). Even if the attenuation coefficient $\alpha$ value can be quite high, the Sabine’s law still allows us to distinguish the phase transition.

An accurate estimation of $RT_{-10\text{dB}}$ value is obtained by applying log-linear curve-fitting process on the averaged envelopes or the Schroeder-like method (Figure 2), over the received signals.

Once $RT_{-10\text{dB}}$ is measured (through curve-fitting) using equation (5), absorption coefficient $A_m$ is estimated and a phase transition of sol-gel can be deduced.

3. Experimental setup and results
The experimental bench is shown in figure 3. The rear face of the aluminum mould has been equipped with a set of 9 identical piezoelectric (PZT) patches to the plate surface to act as sensors. A 10 mm diameter has been chosen for the patches in order to simulate approximately punctual displacements. One of these is used as a source and is powered with an electrical signal provided by an arbitrary function generator (Agilent 33220a). This electrical signal is set to a 10 V amplitude and corresponds to one 300 kHz sine cycle. This particular frequency range was chosen to privilege bulk acoustic waves (wavelength smaller than the dimensions of the aluminum

![Figure 1. Aluminum mould and sol-gel cavity.](image-url)
Figure 2. Experimental results: Schroeder’s integrals average over the received signals (—) and the fitted curve (— —).

mould). The 8 other PZT patches are connected successively to a four-channel oscilloscope (LECROY HDO4104) and are used as receivers. In fact, 1024 signals are acquired over a few seconds and time averaged in order to reduce discretization noise and obtain an improved SNR. Then, the reverberated signals are transferred via the Ethernet bus to a computer for the signal processing step, using Matlab software. Thus, spatial-averaging over 8 receivers is calculated in order to privilege coda waves and attenuate the direct paths propagation.

Figure 3. Experimental setup to estimate reverberation time (RT).

Figure 4 shows a typical reverbrant signal received in a solid medium and represented in time (a) and frequency (b) domain. It can be observed that sufficient modal overlaps occur in the
plate (Figure 4-b), allowing to qualify the field as diffuse.

**Figure 4.** Example of a reverberant signal received in a solid medium, represented in time domain (a) and frequency domain (b).

**Figure 5.** Three characteristic cases of aluminum mould: (a) sol-gel free aluminum mould, (b) sol-gel with low attenuation, (c) sol-gel with high attenuation.

Figure 5 shows the measurement principle using three characteristic cases. In the first case, the measurement is performed only on an aluminum-mould, without sol-gel. Results
show a very low attenuation due to high mechanical impedance mismatching between air and aluminum (Figure 5-a). In the second case, sol-gel is in liquid phase, whereas part of the energy is absorbed by the solution and hence less reverberation in the mould (Figure 5-b). In the third case, the sol-gel is in a solid phase and presents higher absorption due to better impedance matching (figure 5-(c)).

As shown in figure 5, the reverberated signals follow an exponential decay. Thus, RT are estimated through a log-linear curve fitting process applied to Schroeder’s integrals average to deduce $A_m$.

![Figure 6. Experimental result: reverberation time in function of temperature.](image)

In order to validate our principle, the determination of sol-gel phase transition of Salol is studied. Salol ($C_{13}H_{10}O_3$) is a white crystalline powder derived from salicylic acid and used in the manufacture of plastics, suntan oils and in medical application, as an analgesic and antipyretic. The figure 6 shows the variation of the reverberation time as a function of temperature during the cooling phase.

The reverberation time for solid salol is around 0.4 ms whereas it is around 1.8 ms for liquid phase. A smooth variation of this value is observed during the transition phase. Thus, results showed that the RT is directly linked to phase of sol-gel, here salol, and can be used to monitor the phase transition of sol-gels.

4. Conclusion
The presented work establishes a direct relationship between the phase transition of sol-gel and the behavior of the reverberated signals. In addition, used technique used does not require any time measurement or even trigger synchronization between the input channels of instrumentation, and thus implies low hardware requirements. Such methods could also be used to complement conventional NDT techniques and structural health monitoring. The Sabine’s equation is adopted and adapted for aluminum reverberating media in order to estimate phase transition of sol-gel. Experimental validation has been performed on salol and have shown that reverberation time is sensitive to the sol-gel phase variation (salol in our case). Thus, this work shows that room acoustic technique can be applied to solid reverberating media in order to perform non destructive evaluation of complex media such as sol-gel. This method has several advantages compared to other proposed methods in literature (low cost, contactless, non-invasive) and can be easily implemented on the production line. The first experimental
validation, presented in this work, shows that this method is a very promising way to estimate sol-gel transition. Future works will focus on in-situ estimation of other sol-gel parameters, such as viscosity.

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