Scattering of ultrasonic shock waves in suspensions of silica nanoparticles

Michael Baudoin and Jean-Louis Thomas
Institut des NanoSciences de Paris—UMR CNRS 7588, Université Pierre et Marie Curie—Paris 6, 4 place Jussieu, 75252 Paris Cedex 05, France

François Coulouvrat
Institut Jean le Rond d’Alembert—UMR CNRS 7190, Université Pierre et Marie Curie—Paris 6, 4 place Jussieu, 75252 Paris Cedex 05, France

Corinne Chanéac
Laboratoire de Chimie de la Matière Condensée de Paris—UMR CNRS 7574, Université Pierre et Marie Curie – Paris 6, 4 place Jussieu, 75252 Paris Cedex 05, France

(Received 5 February 2010; revised 27 October 2010; accepted 11 December 2010)

Experiments are carried out to assess, for the first time, the validity of a generalized Burgers’ equation, introduced first by Davidson [J. Acoust. Soc. Am. 54, 1331–1342 (1973)] to compute the nonlinear propagation of finite amplitude acoustical waves in suspensions of “rigid” particles. Silica nanoparticles of two sizes (33 and 69 nm) have been synthesized in a water–ethanol mixture and precisely characterized via electron microscopy. An acoustical beam of high amplitude is generated at 1 MHz inside a water tank, leading to the formation of acoustical shock waves through nonlinear steepening. The signal is then measured after propagation in a cylinder containing either a reference solution or suspensions of nanoparticles. In this way, a “nonlinear attenuation” is obtained and compared to the numerical solution of a generalized Burgers’ equation adapted to the case of hydrosols. An excellent agreement (corresponding to an error on the particles size estimation of 3 nm) is achieved in the frequency range from 1 to 40 MHz. Both visco-inertial and thermal scattering are significant in the present case, whereas thermal effects can generally be neglected for most hydrosols. This is due to the value of the specific heat ratio of water–ethanol mixture which significantly differs from unity.

PACS number(s): 43.25.Jh, 43.20.Fn, 43.35.Bf [ROC] Pages: 1209–1220

I. INTRODUCTION

The propagation of finite amplitude acoustic waves in suspensions of “rigid” particles has been first studied theoretically by Davidson in 1973. Contrary to the case of high amplitude hydrodynamic shock waves, simplified equations can be obtained through a rigorous asymptotic matching. This is due to the small amplitude of acoustical shock waves compared to hydrodynamic shock waves. Davidson has derived several generalized Burgers’ equations, with one term due to the nonlinear propagation in the continuous phase, and additional relaxation terms due to momentum, heat, and mass transfers between particles and the surrounding medium. We recall that the usual Burgers’ equation with thermo-viscous absorption has been first introduced in acoustics by Mendousse, for the propagation of finite amplitude acoustic waves in a viscous perfect gas. The notion of generalized Burgers’ equation adapted to any kind of linear dispersion relation is proposed by Blackstock.

A generalized Burgers’ equation for two-phase media can be obtained by averaging and simplifying Navier–Stokes equations, providing that (1) the size $a$ of the particles is much smaller than the acoustical wavelength $\lambda$, (2) the suspension is dilute, and (3) the response of the particles is linear. Otherwise, nonlinear terms are themselves modified by the presence of nonlinear scatterers. Bubbly media are extensively studied examples.

If theoretical aspects (equations, dispersion relation, shock structure, etc.) of the propagation of finite amplitude acoustic waves in suspensions have been widely studied, there is still no experimental evidence of the validity of such equations. This gap can be explained by the difficulty of performing such experiments. The propagation of finite amplitude acoustic waves in aerosols requires first the formation of a stable and precisely controlled aerosol, and then the generation of acoustic shock waves in air. Both requirements are hardly compatible in simple in-laboratory experiments. In the case of hydrosol, the shock thickness associated with ultrasonic underwater acoustic shock waves is generally about 10 $\mu$m and, therefore, requires the synthesis of suspensions with particles of size within the nano range to meet the above requirements. Recent and tremendous progresses in nanosciences now make this relatively easy to control. We chose to study silica nanoparticles, since particles of controlled and relatively monodisperse size can be simply synthesized. Moreover, the resulting suspension is stable and the particles spatial distribution is statistically homogeneous.
TABLE I. Composition of solutions I and II.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Solution I</th>
<th>Solution II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspension A</td>
<td>30 ml TEOS + 30 ml C₂H₅OH</td>
<td>138 ml C₂H₅OH + 27 ml H₂O + 3 ml NH₄OH</td>
</tr>
<tr>
<td>Suspension B</td>
<td>30 ml TEOS + 30 ml C₂H₅OH</td>
<td>138 ml C₂H₅OH + 28.2 ml H₂O + 1.8 ml NH₄OH</td>
</tr>
<tr>
<td>Solution C</td>
<td>30 ml C₂H₅OH</td>
<td>idem susp. A</td>
</tr>
<tr>
<td>Solution D</td>
<td>30 ml C₂H₅OH</td>
<td>idem susp. B</td>
</tr>
</tbody>
</table>

II. EXPERIMENTAL SECTION

A. Nanoparticles synthesis

Two colloidal suspensions A and B of silica nanoparticles diluted in ethanol with different particle sizes have been synthesized following Stöber process. This is an ammonia-catalyzed condensation reaction of tetraethylorthosilicate (TEOS) [Si(OR)₄ with R = C₂H₅] in ethanol (ROH). A first hydrolysis reaction produces the monomer [(OR)₃Si(OH)]

\[ \text{Si(OR)₄ + H₂O} \rightarrow (\text{OR})₃\text{Si(OH)} + \text{ROH}. \]

Then this monomer condenses to form silica particles:

\[ (\text{OR})₃\text{Si(OH)} + \text{H₂O} \rightarrow \text{SiO₂↓ + 3ROH}. \]

This synthesis is obtained at room temperature by mixing two solutions, a first solution (solution I) of TEOS diluted in water and a second one (solution II) of TEOS, ethanol, and ammonia according to quantities given in Table I. Although this synthesis is widely used, the exact mechanism of growth of the particles is still a controversial issue. The particles growth is statistically isotropic, resulting in relatively spherical particles (except for the smallest particles). The size of the particles is controlled by the pH of the solution and, therefore, the concentration of ammonia. The produced particles are relatively monodisperse, depending, however, if the pH is constant throughout the addition of solution I in solution II. Two additional reference solutions C and D have been prepared by adding the same quantities of water, ethanol, and ammonia as in suspensions A and B, respectively, but without TEOS, hence without particles. Table I sums up the content of the different solutions. The solutions used in our experiments are Carlo Erba ammonia solution 30 wt. % (ρₐm = 892 kg m⁻³, Mₐm = 17 g mol⁻¹), Normapur absolute ethanol solution (ρₐth = 789 kg m⁻³, Mₐm = 46 g mol⁻¹), and Prolabo TEOS solution (ρₐTEOS = 934 kg m⁻³, MₐTEOS = 208 g mol⁻¹), where ρₐ is the density and Mₐ is the molar mass.

Finally, as the presence of bubbles can strongly influence the propagation of acoustical waves, the solutions have been carefully degassed in a vacuum chamber.

B. Composition and physical properties of the suspensions

Surface electrical charges prevent the particles from aggregation, and the particles spatial distribution has been considered as statistically homogeneous due to Brownian motion. Indeed, the characteristic length Lₖ of sedimentation on a time scale Δt is equal for a dilute suspension to

\[ Lₖ = \frac{2\pi\rho₂Δt}{\rhoₐ\rhoₙgΔt}, \]

where a is the size of the particles, ρ₂, the viscosity of the liquid, ρₐ and ρₙ the densities of the continuous and dispersed phase, and g the standard gravity. At the same time, due to Brownian motion, particles will explore a zone whose characteristic size is

\[ Lₖ = \sqrt{\frac{kₜ T}{6πₙ₉qₙΔt}}, \]

where kₜ is the Boltzmann constant and T is the temperature. In this case, the suspensions were mixed with a magnetic stirrer while degassing. Then the experiment was carried out within the day, which means that the characteristic time Δt is <86 400 s. If we report Δt in the above formula, we obtain Lₖ ~ 2 mm. Thus, sedimentation is weak and counteracted by Brownian motion which shuffles the suspension.

During the synthesis, some TEOS and water molecules are consumed and some ethanol molecules and silica nanoparticles are formed. We can compute the mass content of the final solutions, if we suppose that all TEOS molecules have reacted (see Table II). Indeed, Bogush et al. have studied the kinetics of Stöber process. They have shown that all TEOS molecules are consumed during the chemical reaction and that soluble silica (that is, silica that is not condensed into particles) represents at most 0.6% of the silica introduced in the reaction. The percentages given in parenthesis in Table II correspond to the mass fraction of each component of the liquid phase.

The composition of the reference solutions C and D slightly differs from the one of liquid phase in the corresponding

<table>
<thead>
<tr>
<th></th>
<th>C₂H₅OH(g)</th>
<th>H₂O(g)</th>
<th>NH₄(g)</th>
<th>SiO₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspension A (%)</td>
<td>157.3 (86.4)</td>
<td>23.9 (13.2)</td>
<td>0.8 (0.4)</td>
<td>8.1</td>
</tr>
<tr>
<td>Suspension B (%)</td>
<td>157.3 (86.3)</td>
<td>24.4 (13.4)</td>
<td>0.3 (0.3)</td>
<td>8.1</td>
</tr>
<tr>
<td>Solution C (%)</td>
<td>132.6 (81.8)</td>
<td>28.8 (17.7)</td>
<td>2.7 (0.5)</td>
<td>0</td>
</tr>
<tr>
<td>Solution D (%)</td>
<td>132.6 (81.7)</td>
<td>29.2 (18)</td>
<td>1.6 (0.3)</td>
<td>0</td>
</tr>
</tbody>
</table>
suspensions, as we did not consider the chemical reactions (which consume water and produce ethanol) when preparing them. The properties of the liquid phase used for the comparison of our simulations with experiments are summed up in Table III.

The sound speeds $c_{\text{so}}$ for each solution have been determined by measuring the flight time in the different solutions. The nonlinear parameter in a water–ethanol mixture (with concentrations of ethanol ranging from 0 to 100%) has been measured by Jacob et al.\textsuperscript{17} and Emery et al.,\textsuperscript{18} respectively, at 27 °C and 20 °C. We can note that the shear viscosity of a water–ethanol mixture is much higher than that of pure water or ethanol solution, even for a small amount of water.\textsuperscript{19} The excess density of the mixing is also strongly dependent on the proportion of water and ethanol. This is due to the formation of hydrogen bonds\textsuperscript{20} between water and alcohol molecules. Finally, it is interesting to note that unlike most liquids; the specific heat ratio $\gamma_c$ of ethanol (and consequently ethanol–water mixture) is significantly higher than 1, that is, there is a difference between the isochoric and isobaric heat capacities. If $(\gamma_c - 1) = 6 \times 10^{-3}$ for water, it is, however, approximately equal to 0.15 for our suspensions, that is, 25 times higher. This will play a fundamental role in our suspensions as the temperature variations associated with the acoustic wave, which are proportional to $(\gamma_c - 1)$, cannot be neglected, contrary to most hydrosols.

The only relevant physical properties of the particles for our model are their size, density, heat capacity, and the volume fraction that they occupy. The size distribution of the particles has been determined from images obtained by transmission electron microscopy (TEM). TEM sample was obtained by the deposition of a drop of our suspensions on a carbon coated grid. The relatively monodisperse size of the particles has been fitted to a log normal law (cf. Fig. 1) of the form

$$\Phi(a) = \frac{\exp(-1/2[(\ln(a) - m)/s]^2)}{a\sigma\sqrt{2\pi}},$$

where $\Phi(a)$ is the volume occupied by the particles of size between $a$ and $a + da$, relative to the total volume occupied by the particles. Here $m$ and $s$ are two constants calculated by a best fit process. The average radius of the suspension is related to these parameters according to the law:

$$a_{\text{moy}} = \exp(m + s^2/2).$$

For suspension A the average radius is 69 nm and for suspension B, it is 33 nm.

The density of silicon dioxide strongly depends on its molecular structure and porosity. Several authors (see Labrosse and Burneau\textsuperscript{21} for a review) have estimated the density of “dry” particles, from measurement of the particles size and the mass of the suspension after evaporation of the liquid phase. The reported values lie in the range from 1980 to 2100 kg m$^{-3}$. However, silica nanoparticles are porous with a fractal structure, as demonstrated experimentally by Labrosse and Burneau\textsuperscript{21} and Szekeres et al.,\textsuperscript{22} Thus, the final

<table>
<thead>
<tr>
<th>TABLE III. Physical properties of the liquid phase (at 18 °C).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Sound speed $c_{\text{so}}$ (ms$^{-1}$)</td>
</tr>
<tr>
<td>Nonlinear parameter $\beta_d$ (Ref. 17)</td>
</tr>
<tr>
<td>Shear viscosity $\mu_\alpha$ ($10^{-3}$ kg m$^{-1}$ s$^{-1}$)</td>
</tr>
<tr>
<td>Bulk viscosity $\mu_\beta$ ($10^{-3}$ kg m$^{-1}$ s$^{-1}$)</td>
</tr>
<tr>
<td>Density $\rho_{\text{so}}$ ($10^{-3}$ kg m$^{-3}$)</td>
</tr>
<tr>
<td>Isobaric heat capacity $C_p(J$ kg$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>Isochoric heat capacity $C_v(J$ kg$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>Specific heat ratio $\gamma_c$</td>
</tr>
<tr>
<td>Thermal conductivity $k_c(W$ m$^{-1}$ K$^{-1}$)</td>
</tr>
</tbody>
</table>

*Measured by the authors.

The evolution of the bulk viscosity with temperature is assumed to follow the same law as the shear viscosity.
mass of “dried” particles depends on how well the particles have been dried. Indeed, the liquid in the largest pores can evaporate even at room temperature. In intermediate pores, the liquid is trapped and can only evaporate if the temperature is increased above the fusion point of water. Finally, there is also some structural water which remains even when the temperature is increased up to 100 °C. Thus, it is not surprising that discrepancies are reported on the density of “dry” particles, depending on the methods of preparation and measurement. However, in acoustical problems, the density of interest is the density of “wet” nanoparticles. From our knowledge, the only reported value of this wet density comes from acoustical measurement. Hipp et al. have measured the linear attenuation of acoustic waves induced by suspension of silica nanoparticles for a large range of frequencies, particle numbers, and concentrations. Their results show a very good agreement between theory and experiments (in the dilute case) for a density of 2200 kg m⁻³. Since the attenuation is relatively sensitive to this parameter, a wrong value of silica density would have resulted in large discrepancies in their comparison between theory and experiments. This work, therefore, provides an excellent characterization of this parameter. We, therefore, used this value of silica density in our computations.

Finally, the volume fraction occupied by the particles has been computed from the density of the particles and the total mass of silica present in the suspension. Table IV sums up the properties of the dispersed phase. From these data, we can compute the mass fraction  \( m = \frac{\rho_{do}}{\rho_{co}} = 4.5 \times 10^{-2} \).

<table>
<thead>
<tr>
<th>Density ( \rho_{do} ) (kg m⁻³)</th>
<th>Volume(^a) fraction ( z_{do} )</th>
<th>Heat capacity ( C_v ) (J kg⁻¹ K⁻¹)</th>
<th>Therm. conduct. ( \lambda_c ) (W m⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2200</td>
<td>1.65%</td>
<td>727</td>
<td>1.05</td>
</tr>
</tbody>
</table>

\(^a\)Measured by the authors.

C. Shock wave generation

A sketch of the acoustical experimental setup is represented in Fig. 2. A high amplitude acoustical wave (\( P_a = 0.41 \) MPa) is emitted at a frequency of \( \omega/2\pi = 1 \) MHz in a water tank by an array of 256 piezoelectric transducers controlled by a programmable electronics of 128 channels. The transmitted code on each channel is computed with the inverse filter method in order to synthesize within a control plane and the requested spatial wave pattern, a plane wavefront with Gaussian amplitude. A cylindrical cell with lateral poly(methyl methacrylate) (PMMA) walls containing either the suspension or a reference solution (without particles) is set 35 cm away from the array, while the shock formation distance in water is equal to \( \rho_{co}/(\rho_{co}P_a) = 37 \) cm, where \( \rho_{co}, C_v, \) and \( \beta_v \) are, respectively, the density, sound speed, and nonlinear parameter of water. The shell is 5.87 cm long and has a radius of 3 cm. Solutions are isolated from water by two lateral mylar membranes, which are approximately acoustically transparent but slightly filter the signal, as detailed later.

Through the inverse filter technique, the wavefront shape has been optimized in order to minimize any effects, but the scattering by the particles. A wavefront as plane and broad as possible was synthesized to minimize diffraction, but smaller than 3 cm, in order to minimize the scattering of the acoustical wave by the PMMA walls of the cell. The decrease of the amplitude of the Gaussian beam edge was sufficiently smooth to minimize the interferences between edges and direct waves from the array. Even though the inverse filter is linear and, hence, performed first at low amplitudes, it is very stable to strong nonlinear effects (see Marchiano et al.). The quality of the synthesis is assessed by Figs. 3 and 4, which show the spatial and temporal shape of the signal measured on a rectangular grid at the entrance of the cylinder. All the measurements are made by moving a membrane hydrophone with a three axis linear stages. The spatial step is fixed to 2 mm on both transverse directions. A strongly steepened signal with a broad harmonic content is visible in Figs. 3(a)–3(c). Figure 3(d) shows the amplitude distribution in the transverse plane after band-pass filtering of the fundamental mode at 1 MHz. Contour plots at –3, –6, and –12dB have been superimposed to emphasize the smooth decrease of the limited aperture of wavefront along this transverse plane. To assess the planarity of the wavefront, the pressure measured on two perpendicular lines crossing at the center of the beam is shown in Figs. 4(a) and 4(b), respectively. The half peak-to-peak maximum amplitude is presented in Figs. 4(c) and 4(d). The smooth decrease on the edge is clearly visible in both directions. These measurements are affected by a relative uncertainty due to the impulse response of the hydrophone. The hydrophone bandwidth is constructor calibrated for frequencies spanning from 1 to 30 MHz. This calibration is performed for the amplitude only and emphasizes the membrane resonance around 30 MHz due to its finite thickness. However, the relative phase between the harmonics is also affected by this
resonance and is responsible for severe distortion of the signal. To mitigate these effects and obtain the signal presented in Fig. 3, a home-made calibration of amplitude and phase up to 60 MHz was performed. This calibration consists in removing the bell shape variation of phase and amplitude around the resonance frequency. It is important to note, however, that these calibrations are subject to a relative uncertainty. Hence, as will be explained below, the acoustic spectroscopy uses a reference solution to get relative measurements independent of the impulse response of the hydrophone.

Finally, the acoustic wave is measured 15 mm behind the cylinder. Despite our careful design of the experiment, some small side effects are observed. The first one is the diffraction of the acoustic beam by the lateral walls of the cylindrical cell. This effect is visible in Fig. 5, where we see the interference rings on the spatial scan [Fig. 5(b)], and the effects on the temporal signal [Fig. 5(a)].

As the distance covered by the edge wave is higher than the one covered by the direct wave, the expected delay given by the geometry is

$$\tau = \frac{\sqrt{3^2 + (5.8 + 1.5)^2} - (5.8 + 1.5)}{12000/2700 - 5 \times 10^{-6}} \approx 5 \times 10^{-6}$$

that is, about five periods of the signal (for a measurement on the central axis of the cylinder). We effectively see in Fig. 5(a) (black line), the disturbance appearing about five periods after the beginning of the signal. To minimize this effect, we selected nine spatial locations within the measurement plane, separated from one another by a step of 2 mm and located at the nearest of the propagation axis. Since the scattered wave varies with the measurement point, contrarily to the plane wave, the averaging on these nine locations reduces this adverse effect [see the gray line in Fig. 5(a)]. The second effect (the radiation of acoustic wave by the PMMA) will, on the contrary, affect the beginning of the signal as the sound speed in PMMA (∼2700 m/s) is higher than the one in our solution (∼1200 m/s).
Nevertheless both phenomena will mainly affect the first harmonics, as higher harmonics result from nonlinear interaction between first harmonics so that their beam widths are narrower and thus significantly smaller than the cell width (see Fig. 6). Another solution would have been to build a larger cell that would have required a larger volume of solution to fill it. Taking into account the small final impact after spatial averaging, and affecting only the low frequency part of the extra-attenuation measurements, this possibility was disregarded.

III. THEORY

A. Extended Burgers’ equation

A generalized Burgers’ equation can be used to describe the propagation of finite amplitude acoustical waves in suspensions as demonstrated first by Davidson.\textsuperscript{1,2} This equation, obtained by perturbation methods, takes into account the nonlinear effects due to the high amplitude of the impinging wave, scattering effects due to the presence of particles, and classical thermo-viscous dissipation within the continuous phase. They rely on the assumption that the smallest scale associated with the acoustic wave (here the shock thickness) is much larger than the particles. With this hypothesis, the equations can be statistically averaged over the particle configurations, and the medium can be considered as an effective medium. The “geometrical” diffraction of the wave by the particles can also be neglected. This hypothesis is well verified in our experiments, as the sizes of our particles are smaller than 70 nm and the shock thickness is about 10 \textmu m in our case. The validity of these equations is also limited to dilute suspensions, as interactions\textsuperscript{23,27,28} between particles are neglected. Davidson has obtained equations for the nonlinear propagation of acoustical waves in aerosols. His results have been generalized by Baudoin\textsuperscript{4} for any dilute suspension of spherical rigid particles, that is, for aerosols and also for hydrosols. These two cases differ in terms of the dominant scattering mechanism. In hydrosols, the scattering of the incident wave is usually due to the steady and unsteady momentum transfers induced at small scales by the difference of velocity between the particles and the surrounding medium. The force exerted by the fluid on the particles at these small scales (and, therefore, small associated Reynolds number) can be obtained by considering a moving sphere embedded in a uniform and unsteady velocity field. Uniform field approximation is justified by the small size of the particles relative to the acoustical wavelength. The result is the sum of the Stokes, Basset, Added mass, and Archimed forces.\textsuperscript{29} The first term is the classic Stokes drag exerted on a sphere embedded in a steady viscous flow. The Basset hereditary force is an unsteady viscous term due to the time required by the viscous diffusion layer to adapt to new boundary conditions. The Added mass term is linked to the inertia of the liquid, which must be displaced when a sphere

![FIG. 5.](image1.png) (Color online) (a) Temporal waveform of the signal measured at the exit of the cylinder before (black line) and after (gray line) averaging. (b) Amplitude (in MPa) of the first harmonic over the beam cross section. Rings are due to the interferences between the direct wave and the signal diffracted at the edge of the cylinder.

![FIG. 6.](image2.png) (Color online) Spatial extension of acoustic beam. Cross section at the entrance of the cylinder: (a) the tenth harmonic and (b) the twentieth harmonic. Cross section at the exit of the cylinder: (c) the tenth harmonic and (d) the twentieth harmonic. Colorbar: amplitude in kPa.
is accelerated or decelerated. Finally the Archimed force is an unsteady inertial force that comes from the difference of density between the particles and the surrounding medium. An additional term is due to the difference of compressibility between the liquid and the particles, which affects the phase velocity but not the attenuation. Thermal exchanges can usually be neglected in hydrosols, as the elevation of temperature associated with the acoustical wave in fluids is proportional to $\gamma_c - 1$, which is very small for most liquids. However, these effects cannot be neglected in the present case, because water–ethanol mixture has a specific heat ratio equal to 1.15. Therefore additional scattering effects arise from steady and unsteady heat transfers between particles and the ambient fluid. The steady term corresponds to the usual Fourier diffusion law for heat transfers between two medium at different temperatures. The unsteady term is the equivalent of the Basset contribution for heat transfers. In the following equations, the temperature inside the particle is assumed to be homogeneous. Indeed, the thermal conductivity of amorphous silica is about five times higher than that of the conductivity of water–ethanol mixture. Hence the diffusion times inside the particles $\tau_d = a^2 \rho_d / C_l / \lambda_d$ are equal to 8 and 2 ns for particles of 69 and 33 nm, respectively, that is, much smaller times than the ones associated with the main harmonics studied here (1 – 40 MHz), which carry most of the acoustical energy.

If we take into account all relevant effects for hydrosols, we obtain the following set of equations:

\[
\frac{\partial \nu_c}{\partial t} - \frac{\beta_{nl}}{c_{co}^2} \left( \nu_c \frac{\partial \nu_c}{\partial t} \right) - \Theta \frac{\partial^2 \nu_c}{\partial t^2} = - \frac{m}{2c_{co}} \left[ (1 - r) \frac{\partial \nu_c}{\partial t} - \frac{\partial \Delta v}{\partial t} \right] + \frac{F}{2c_{co}} \left[ \frac{\partial \nu_c}{\partial t} - \frac{\partial \Delta v}{\partial t} \right] - \frac{mC(\gamma_c - 1)}{2c_{co}} \left[ \frac{\partial \nu_c}{\partial t} - \frac{\rho_c}{c_{co}} \frac{\partial \Delta T}{\partial t} \right].
\]

(1)

\[
(1 - r) \frac{\partial \nu_c}{\partial t} - \frac{\partial \Delta v}{\partial t} = \frac{1}{\tau_v} \left[ \Delta v + \frac{0_c}{\gamma_c} \frac{\partial \Delta v}{\partial t} + \sqrt{\frac{0_c}{\pi}} \left[ \frac{\partial \Delta v}{\partial t^*} \right] \right].
\]

(2)

\[
\frac{\rho_c}{c_{co}} \frac{\partial \Delta T}{\partial t} = \frac{1}{\tau_T} \left[ \Delta T + \sqrt{\frac{0_c}{\pi}} \left[ \frac{\partial \Delta T}{\partial t^*} \right] \right].
\]

(3)

In the above equations the subscripts “c,” “d,” and “o” denote, respectively, the continuous fluid phase, the dispersed phase (particles), and the equilibrium state. $\nu_c$ is the mean velocity of the continuous phase, $\Delta v$ is the velocity difference between the two phases, $T_c$ is the mean temperature of the continuous phase. $\Delta T$ is the temperature difference between the two phases, $s_c$ is the entropy of the continuous phase, $\tau = t - x/c_{co}$ is the retarded time, $\beta_{nl}$ is the coefficient of nonlinearity, $F = \zeta_d / \zeta_{co}$ is the ratio of volume fractions occupied by both phases, $r = \rho_{co} / \rho_{do}$ is the ratio of densities, $m = \zeta_{do} / \zeta_{co} \rho_{co}$ is the mass fraction, $C = C_l / C_o$ is the ratio of isobaric heat capacities of both phases, $\Theta = \nu_l / 2 \rho_{co} C_{co} (4 / 3 + \nu_l / \nu_l + (\gamma_c - 1) / \Pr)$ is the characteristic time for classical thermo-viscous dissipation, and $Pr = \nu_l C_l / \lambda_c$ is the fluid Prandtl number. Finally $\tau_v = a^2 \rho_d / \nu_l$ and $\tau_T = a^2 \rho_d C_l / \lambda_c$ are the characteristic times for the steady and unsteady momentum exchanges, and $\tau_T = a^2 \rho_d C_l / \lambda_c$ are the characteristic times for the steady and unsteady heat transfers.

The first equation is the generalized Burgers’ equation, with usual Burgers’ equation \cite{7,31} on the left-hand side. The three terms correspond, respectively, to the propagation of the acoustic wave, nonlinear effects, and thermo-viscous absorption. The first term on the right-hand side (rhs) corresponds to steady and unsteady momentum exchanges between the two phases. The contribution of this term is proportional to the mass fraction $m$, that is, the product of the densities ratio and the volume fraction ratio: the more the particles and the higher the density ratio, the higher will be the scattering of the impinging wave. The second term on the rhs is a contribution due to the incompressibility of the rigid particles, which therefore modifies the sound speed of the effective medium. The third term on the rhs corresponds to steady and unsteady heat transfers between the particles and the surrounding medium. These exchanges are proportional to $mc$, which characterizes the thermal inertia of the particles versus temperature changes. It is also proportional to $(\gamma_c - 1)$ which gives the amplitude of temperature variations associated with the acoustical wave.

Two additional equations [Eqs. (2) and (3)] are required to determine, respectively, the velocity and temperature differences between the fluid and solid phases. In the first Eq. (2), we can see that, if the particles have the same density as the surrounding liquid ($r = 1$), the velocity difference between the phases vanishes and the particles, therefore, will move with the same velocity as the surrounding liquid. That is why particles of the same density as the liquid are used for particle image velocimetry (PIV) in hydrodynamic studies. In this case, there is no scattering of the impinging wave. This factor $(1 - r)$ comes from the Archimed force. The first term of the rhs is the Stokes contribution, the second the Added mass, and the last one the Basset history term. As underlined before, we see that the Stokes term is a steady contribution proportional to the velocity difference $\Delta v$ between the two phases, whereas Added mass and Basset are unsteady terms therefore related to the time derivative of the velocity. The Basset term depends on the “history” of the particle displacement through the time integral. Equation (3) shares the same structure as Eq. (2), but without the Archimed and Added mass terms. Compared to the equations obtained by Davidson \cite{2,6} for aerosols, Eqs. (1)–(3) take into account unsteady momentum and heat transfers. These effects play a fundamental role in hydrosols, whereas they can be neglected in most practical situations in aerosols. The ratio between unsteady and steady characteristic times of momentum and heat transfers is indeed, respectively, equal to $9/2r$ and $3rC$. In hydrosols, the density and specific heat of the dispersed and continuous phases are close. As a result,
unsteady and steady scattering phenomena occur at the same frequencies. In the case of aerosols, however, unsteady transfers occur at much higher frequency due to the huge difference of density between both phases. Therefore, unsteady transfers play a minor role, even when considering the propagation of acoustical shock waves.

B. Analysis based on characteristic parameters

In this section, we will try to compare the different terms and understand which one is significant in the present case. If we try to compare momentum transfers to heat transfers, we see that both are proportional to the mass fraction $m$, but that the heat transfers are also proportional to $C(\gamma - 1)$. This factor is approximately equal to $4 \times 10^{-2}$ in our suspensions. Only based on this first comparison, we might think that thermal effects can be neglected compared to visco-inertial ones. However, the characteristic frequencies of both phenomena also differ. Table V sums up the characteristic frequencies for suspensions A and B.

These characteristic frequencies must be compared to the frequency spectrum (~1 to 40 MHz) associated with the shock wave. We can see that characteristic frequencies associated with thermal transfers are much smaller than their momentum number is also small, and viscous effects play a major role in the dynamics of the particles. Therefore, the differential movement between both phases is damped by viscous effects, so that part of the energy carried out by the acoustical wave is dissipated. In the same way, some energy is dissipated through heat diffusion because of the difference of temperature between the phases. If we look at the phase velocity of the effective medium, it can be estimated as $c_{eff} = \frac{1}{\sqrt{\rho_{eff} \lambda_{eff}}}$, where $\rho_{eff}$ is the effective density and $\lambda_{eff}$ is the effective compressibility. If the particles have the same temperature and velocity as the liquid, the effective phase velocity will, nevertheless, globally shift because of the increase of the effective density (particles are denser than the surrounding liquid) and the decrease of the compressibility (particles are much less compressible than the surrounding liquid). Figure 7 shows that the increase of the effective density is dominant, as the effective phase velocity globally decreases when we take into account the presence of the particles. On the other hand, the evolution of the effective phase velocity with frequency is due to the velocity and temperature differences between both phases. Of course the classical thermo-viscous dissipation does not affect the phase velocity, but only induces attenuation.

C. Transmission and reflection coefficients

The extremities of the cylinder containing the suspension or the reference solution are mylar membranes. Their thickness (measured with a micrometer directly on the experimental setup) is 13 µm. As a consequence, these membranes are transparent for the lowest harmonics of the acoustic shock wave but slightly filter the highest harmonics. The transmission coefficient can be simply calculated for the first and second membrane from the acoustic impedance of each material and the thickness of the membrane. We get:

\[
T = \frac{2}{1 + \frac{2}{\pi} \cos(k_2 h) - i \left( \frac{2}{\pi} + \frac{2}{\pi} \right) \sin(k_2 h)},
\]

\[
k_s c_{co} = \omega \phi_s + \frac{i \omega \mu_s}{2 \rho_{co} c_{co}^2} \left( 4 \mu_s^2 + (\gamma_s - 1) \phi_s \right) + m \frac{(1 - r) h_r}{2} + \frac{m C(\gamma_r - 1)}{2} h_{rt}
\]

\[
h_r = \frac{1 - i \omega \tau_{tr}^s}{1 - i \omega \tau_{tr}^s}, \quad h_{rt} = \frac{1}{1 - i \omega \tau_{tr}^t}
\]

\[
\tau_{tr}^s = \tau_{tr} S \left( 1 + \frac{1 - i}{\sqrt{2}} (\omega h_r)^{1/2} - \frac{1}{9} i \omega h_r \right),
\]

\[
\tau_{tr}^t = \tau_{tr} T \left( 1 + \frac{1 - i}{\sqrt{2}} (\omega h_r)^{1/2} \right).
\]

The first term on the rhs of Eq. (4) is due to the presence of incompressible particles, the second one correspond to classical thermo-viscous dissipation, the third one to momentum transfers between both phases, and the last one to thermal transfers. The complex times $\tau_r^s$ and $\tau_r^t$ are linked, respectively, to momentum and thermal transfers. We can note that this dispersion relation is equivalent to the one calculated in the linear case by Gumerov et al. in the small volume fraction limit, without phase changes and when the temperature inside the particles is supposed to be homogeneous.

The presence of particles induces viscous damping of the acoustic wave because of the difference of velocity between the particles and the fluid, and the small size of the particles. As the particles are small, the associated Reynolds number is also small, and viscous effects play a major role in the dynamics of the particles. Therefore, the differential movement between both phases is damped by viscous effects, so that part of the energy carried out by the acoustical wave is dissipated. In the same way, some energy is dissipated through heat diffusion because of the difference of temperature between the phases. If we look at the phase velocity of the effective medium, it can be estimated as $c_{eff} = \frac{1}{\sqrt{\rho_{eff} \lambda_{eff}}}$, where $\rho_{eff}$ is the effective density and $\lambda_{eff}$ is the effective compressibility. If the particles have the same temperature and velocity as the liquid, the effective phase velocity will, nevertheless, globally shift because of the increase of the effective density (particles are denser than the surrounding liquid) and the decrease of the compressibility (particles are much less compressible than the surrounding liquid). Figure 7 shows that the increase of the effective density is dominant, as the effective phase velocity globally decreases when we take into account the presence of the particles. On the other hand, the evolution of the effective phase velocity with frequency is due to the velocity and temperature differences between both phases. Of course the classical thermo-viscous dissipation does not affect the phase velocity, but only induces attenuation.

C. Transmission and reflection coefficients

The extremities of the cylinder containing the suspension or the reference solution are mylar membranes. Their thickness (measured with a micrometer directly on the experimental setup) is 13 µm. As a consequence, these membranes are transparent for the lowest harmonics of the acoustic shock wave but slightly filter the highest harmonics. The transmission coefficient can be simply calculated for the first and second membrane from the acoustic impedance of each material and the thickness of the membrane. We get:

\[
T = \frac{2}{1 + \frac{2}{\pi} \cos(k_2 h) - i \left( \frac{2}{\pi} + \frac{2}{\pi} \right) \sin(k_2 h)},
\]
where $T$ is the transmission coefficient; $Z_1$, $Z_2$, and $Z_3$ are, respectively, the acoustic impedance of the liquid before the membrane, the membrane, and the liquid after the membrane, $k_2$ is the wave number in the mylar membrane, and $h$ the thickness of the membrane. For our calculations, we took the following properties of mylar membrane (Ref. 32): $\rho_{\text{myl}} = 1180 \text{ kgm}^{-3}$ and $c_{\text{myl}} = 2540 \text{ ms}^{-1}$. With this formula, we can see that if the membrane is sufficiently thin (that is, $k_2 h \ll 1$), the transmission coefficient is equal to $T = 2Z_3/(Z_3 + Z_1)$, so that the membrane plays no role. In our case $k_2 h \approx 0.04$ at 1 MHz and equal to 4 at 100 MHz. Therefore, the membrane will mainly affect the highest harmonics. The transmission coefficient modulus for the first and second membrane is represented in Fig. 8.

D. Computation scheme

Equations (1)–(3) are solved by using a split step numerical scheme. Advancing plane-by-plane from position $x$ to position $x + \Delta x$, nonlinear and scattering effects are considered separately through two successive sub-steps. Nonlinear effects are treated with the so called Burgers–Hayes method\(^{33,34}\) that provides an analytical solution for shock waves in the inviscid case for the potential (the primitive of the pressure). The attenuation and dispersion, due to the presence of the particles and to classic thermo-viscous dissipation, are taken into account by applying the appropriate dispersion relation [Eq. (4)] in the frequency domain. Note that the numerical algorithm alternating weak shock theory reformulated for the potential flow in the time domain, and linear dispersion/dissipation handled in the frequency domain is a generalization of Pestorius algorithm.\(^{35}\) It has also been validated for thermoviscosity and molecular relaxation applications to sonic boom.\(^{36}\) Polydispersion can simply be taken into account by replacing $h_V$ and $h_T$ by their values averaged over the particles size distribution\(^{37}\)

$$\langle h_j \rangle_\phi = \int_{\phi_{\text{min}}}^{\phi_{\text{max}}} \phi_j(a) h_j(a) da \quad \text{with } j = v \text{ or } T$$  \hspace{1cm} (6)

We first process the signal measured experimentally at the entrance of the cylinder. This process consists in the calibration and the spatial averaging described in Sec. II C. Then, it is propagated numerically along the same path as the one followed experimentally, that is, linear transmission through the first membrane, 5.87 cm of nonlinear propagation in the reference solution or the suspension, linear transmission through the second membrane, and finally 1.5 cm of nonlinear propagation in water up to the hydrophone position. It is important to note, that our measured entrance signal is given within the uncertainty of our membrane hydrophone calibration for frequencies higher than 20 MHz. This is the reason why the cell location was chosen at the point of shock formation. Here the amplitudes of harmonics above 20 MHz are $-40 \text{ dB}$ less than the fundamental Fig. (3). Most of them will indeed result from nonlinear interaction within the cell (which is enhanced by the larger coefficient of nonlinearity in the water–ethanol mixture). Hence calibration errors above 20 MHz will be negligible when comparing theory and

FIG. 7. Comparison of visco-inertial, thermal, and overall effects due to the presence of the particles with the classical thermo-viscous dissipation in the corresponding liquid. (a) Comparison of attenuation in suspension A (69 nm). (b) Comparison of attenuation in suspension B (33 nm). (c) Comparison of phase velocity in suspension A (69 nm). (d) Comparison of phase velocity in suspension B (33 nm).
experiments for relative quantities between solutions with or without particles.

IV. RESULTS AND ANALYSIS
A. Comparison of temporal signals and their Fourier transforms

In this section, we compare computed and measured signals and their Fourier transforms after propagation in the two suspensions and the corresponding reference solutions (see Figs. 9 and 10). Simulations have been performed with the literature parameters given in Sec. II without any adjustment. A good agreement is obtained between the simulations and the experiments. The direct comparison of measured temporal signals (or their Fourier transforms) with computed ones, however, leads to small discrepancies, which come from side effects such as (1) the uncertainty on the calibration of the membrane hydrophone (for frequencies above 20 MHz) and (2) the diffraction by the walls of the cell.

B. Comparison of “nonlinear” attenuation

The best way to eliminate these side effects is to calculate the ratio between the signals propagated in the suspension and in the reference solution. With this method, a “nonlinear” attenuation is obtained for each harmonic by computing the amplitude of this ratio. It differs from its linear counterpart, as the evolution of the amplitude of the harmonics results from a complex competition between nonlinear effects which transfer energy from the fundamental to the harmonics, and scattering by particles, which tends to dissipate energy. These nonlinear coefficients therefore strongly depend on the distance of propagation through the suspension. We did not compare computed and measured dispersion, as the phase velocity evolution with frequency is very small (about 0.1%) and is within the experimental uncertainties.

Figures 11(a) and 11(b) show the nonlinear attenuation in suspensions A and B, respectively, obtained experimentally and numerically by solving the generalized Burgers’ equation. Computations have been performed for different sizes of particles to give an overview of the influence of this parameter. An excellent agreement is obtained for suspension A for the radius measured from TEM images (69 nm).
For suspension B (radius measured from TEM images of 33 nm), the best agreement with computations is obtained with a particle size of 36 nm, that is, 3 nm (or 10%) difference. The higher discrepancy between experiments and theory for suspension B could be explained by different factors. First, the nonlinear attenuation is much smaller for this suspension; therefore, the measurement noise may more deeply affect the corresponding results. Second, since the structure of silica nanoparticles is fractal according to Szekeres et al., the density might slightly vary with the size of the particles. Finally, the smaller the particles, the higher is the uncertainty on the TEM determination of the particles size. We can notice a small discrepancy for the first harmonics (the attenuation is higher in the experiments). This difference comes from side effects (described earlier in Sec. II) diffraction of a part of the signal at the edge of the cylinder leads to interferences between the direct and edge waves. Finally, we can notice that the variation of the “nonlinear” attenuation with the size of the particles is rather strong. Therefore its measurement is shown to be a good way to acoustically discriminate this parameter, with a precision in our experiments of the order of 3 nm.

C. Comparative influence of different effects

To conclude, we can compare the influence of the different effects induced by the presence of the particles (see Fig. 12). In the absence of particles, the “nonlinear” attenuation of the harmonics is of course negative because the amplitude of the harmonics is increased through the nonlinear transfer of energy from the fundamental to the higher harmonics. First, we can see that taking into account the polydispersion does not significantly affect the results. The calculation of the dispersion relation with the average radius gives, indeed, a correct estimate of the attenuation. This situation differs from the propagation in fogs, where polydispersion plays a crucial role. Figures 12(a) and 12(b) show the strong influence of thermal effects in our suspensions. Although thermal effects are smaller than visco-inertial ones, neglecting them would lead to a huge underestimation of the attenuation in the suspension. Again this is due, in particular, to the relatively high value of the parameter \( \gamma_c - 1 \). Hence, the present experiments allow us to assess the validity of generalized Burgers equations (1)–(3) proposed in the theoretical part of this work. They include simultaneously classical thermoviscosity within the ambient solution, and visco-inertial and thermal transfers between the fluid and the nanoparticles.
V. CONCLUSION

The evolution of an acoustical shock wave propagating in a suspension of silica nanoparticles has been studied experimentally and compared successfully with a generalized Burgers’ equation. This agreement is achieved without any adjustable parameter. Nanoparticles are shown to strongly influence the amplitude and shock structure of the acoustical shock wave. Both visco-inertial effects due to the difference of velocity between the particles and the surrounding liquid, and heat exchanges due to temperature differences, are shown to play a significant role on the acoustical behavior. Finally, we can note that the use of broadband signals such as acoustical shock waves is promising for acoustical spectroscopy. While further investigations would be required to quantify the uncertainty on the particles size estimation, this method might allow to determine the size of the particles with a single signal. This would be interesting to characterize quickly evolving media. Potential applications would be, for example, the in situ measurement of particles growth rate during chemical reactions.