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Acoustic spectroscopy of aerogel precursors

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Abstract We investigate the acoustical properties of silica gels, which are precursors in the aerogel production process. These gels exhibit a strong “ringing gel” behavior, that is they emit a characteristic sound if one knocks against the container. We study this sound emission with a very simple spectroscopic technique and observe resonances which are characteristic for natural frequencies of a cylindrical body. From a fit of the experimental frequency positions

to calculated values, we determine a sound velocity of $c_T = 4$ m/s for a gel sample with porosity $\phi = 97.5\%$. This low sound velocity can only be interpreted as the transverse sound mode predicted by Biot’s theory for sound propagation in porous media.

Key words Acoustic properties · Porous materials · Silica gels · Aerogels

Introduction

Some years ago, Oetter and Hoffmann [1] discovered a strange behavior of a class of gels they were investigating. Their gels emitted a characteristic sound upon hitting the container. Oetter and Hoffmann termed this a “ringing gel” or “humming gel” behavior and established this property in a class of gels consisting of ternary phases of a hydrocarbon, a surfactant, and water. The structure of these phases has been investigated subsequently in detail [2], although the physical explanation of the effect remained rather indeterminate. A similar observation had been reported earlier by Bacri et al. [3], but without mentioning an audible sound emission of their polymer gels.

Recently, we observed the same phenomenon to occur for the precursors of the aerogel process that consist of a highly porous silica network filled with an alkanol. These precursors are frequently called the “wet gel” or alcogel. If the alkanol is removed supercritically, one obtains the aerogel as a rigid, lightweight, and transparent body, where the silica frame contributes only approximately 5% to the total volume.

Having this porous structure in mind, we were tempted to interpret the “ringing gel” effect of the alcogels in terms of Biot’s theory for sound propagation in porous media [4], developed originally for the description of sound propagation in submarine sediments. This theory has been fruitfully applied to explain the elastic properties of gels [5]. A review by Johnson [6] of the theory and its relation to published experimental results is available.

In view of Biot’s theory, we suggest the following explanation for the “ringing gel” behavior. Upon knocking against the container, one excites a shear wave in the gel, opposite to the more familiar compressional waves. A compressional wave is present, too, but has a sound velocity higher by some orders of magnitude. The gel within the container forms a resonant body for the shear wave. These resonances are responsible for the audible sound that can be perceived if one hits the container. This suggestion has been tested experimentally by simple acoustic spectroscopy, which will be introduced in this contribution. We will further report the first quantitative results of these experiments.

In what follows, we will start with a crude outline of the theory involved, followed by a description of our experiments and a concluding outlook.

Sound propagation in porous media

Biot's theory describes phenomenologically the propagation of acoustic waves in a porous, fluid-filled, macroscopically homogeneous and isotropic body. Each volume element of this body experiences an average displacement of the fluid and the solid part, respectively. The respective equations of motion are coupled by viscous, as well as inertial, forces. The macroscopic material properties that enter are the bulk moduli of the fluid (K_f) and the solid (K_s) phase, the bulk modulus K_b of the skeletal frame, the shear modulus G , and the porosity ϕ . For details, we refer the reader to Johnson [6], the notation of which we will follow as closely as possible.

General hydrodynamics predicts a crossover between two distinct regimes that is governed by the viscous skin depth, $\delta = (2\eta/\rho_f\omega)^{1/2}$ [7], with η the viscosity and ρ_f the mass density of the fluid phase; ω is the frequency of a disturbance. For porous media this crossover separates a high-frequency from a low-frequency regime, the crossover frequency $\omega_c = 2\eta/\rho_f a^2$ being related to the average pore size a of the medium. Porous materials exhibit pore sizes of the order of 100 nm and less. Therefore, we are essentially always in the low-frequency regime, indicating that the viscous skin depth is much larger than the characteristic pore size. Furthermore, for gels the skeletal frame is generally much more deformable than the pore fluid. This "gel limit" is identified therefore by K_b , $G \ll K_f$.

Applying these assumptions, the theory predicts the following sound modes in the porous medium.

First, there is a fast compressional mode, which is very much like the sound mode in pure liquids. The sound velocity of this longitudinal mode is given by:

$$c_{FL} = c_0 \left[1 + \frac{\xi_1 K_b + \xi_2 G}{2K_f} \right] \quad (1)$$

where $c_0^2 = K_m/\rho_m$ is Wood's result [8] for the sound velocity in a composite medium with $K_b = G = 0$, such as a dispersion of air bubbles in water, or a colloidal suspension. The bulk modulus of the composite medium can be calculated assuming two different elastic media in parallel, yielding for our case $K_m^{-1} = \phi/K_f + (1-\phi)/K_s$. The total density is $\rho_m = \phi\rho_f + (1-\phi)\rho_s$. The ξ_i in Eq. (1) represent the deviations from Wood's formula owing to the finite stiffness of the frame: $\xi_1 = \phi^2(K_m K_f)(K_f^{-1} - K_s^{-1})^2$ and $\xi_2 = \frac{4}{3}K_f/K_m$. The sound attenuation can be calculated correspondingly, but is of little interest in the present context. The compressional mode treated so far can be visualized as a cooperative in-phase motion of fluid and skeletal frame.

Second, there exists a slow compressional mode, corresponding to the out-of-phase motion of fluid and skeleton. The sound velocity of this wave is purely imaginary:

$$c_{SL}^2 = -i\omega \frac{k(K_b + \frac{4}{3}G)}{\eta} \quad (2)$$

corresponding to an overdamped sound mode; k is the permeability defined through Darcy's law $Q = -(kA/\eta)\nabla p$, which relates the volume flow rate Q through a sample area A due to an applied hydrostatic pressure gradient ∇p . Equation (2) can be used to calculate elastic constants of gels from linewidth measurements by dynamic light scattering, as first performed by Tanaka et al. [9].

Third, there is only one trivial shear mode, corresponding to the in-phase movement of fluid and skeleton. The sound velocity of this transversal wave is given by:

$$c_T = \left(\frac{G}{\rho_m} \right)^{1/2} \quad (3)$$

Accordingly, from theory one expects two propagating sound modes in porous media with different sound velocities, which are determined by Eqs. (1) and (3).

Notice that from the "gel limit" $G \ll K_f$, as mentioned above, one can already estimate that the longitudinal sound velocity c_{FL} should be some orders of magnitude higher than the transversal one, c_T .

Materials and methods

Materials

The gels under investigation are prepared by base-catalyzed hydrolysis of tetramethoxysilane (TMOS) in the presence of a large amount of methanol. We use an aqueous solution of 0.1 mol/dm³ ammonia as hydrolyzing agent. The molar ratio of water to TMOS is chosen to 4:1, which is two times the stoichiometric amount. For a gel sample with porosity of nominal $\phi = 97.5\%$, we use 82.6 cm³ methanol. Half of this amount is mixed with 12.5 cm³ TMOS; the remaining amount is mixed with 6.1 cm³ of the aqueous ammonia solution. The aqueous solution is added dropwise to the stirred TMOS solution at room temperature. After some minutes of further stirring, the liquid is filled into cylindrical glass vials with plastic snap-in lids. All reagents are of grade "purum" and were used without further treatment. TMOS is stored under Ar atmosphere.

Gelation occurs for this composition within approximately 12 h. The composition has been chosen to yield the highest porous material within acceptable gelation times.

The gels are known to exhibit an aging behavior. Accordingly, the samples under study were stored approximately one week at room temperature before use.

Experimental setup

For the acoustic spectroscopy, we use a small condenser microphone capsule (Conrad Electronic), which is equipped with an amplifier and a load resistor within the metal housing. Power is provided by an external 3 V battery. The data sheet shows a linear response over almost the whole frequency range of 20–18000 Hz. The microphone output is AC coupled to the high impedance input of a digital oscilloscope (LeCroy 9314). The oscilloscope performs a fast Fourier transformation (FFT) of 5000 data points of the

signal trace. The Nyquist frequency was 2.5 kHz, yielding a frequency step of 1 Hz. The FFT was calculated using a Hamming window, which results in an only slightly poorer frequency resolution of 1.4 Hz. Thirty FFT sweeps are averaged to yield the final spectrogram.

The experimental procedure is as follows. The glass vial is brought into contact with the condenser microphone, the vial being held by hand at its plastic lid. The glass is hit with a metallic screwdriver to excite the sound modes of the gel. The oscilloscope is pre-triggered onto this signal with a delay of 0.05 s, the time-base being 0.1 s. These settings assure that the acoustic signal is dominated by the sound modes of the gel, the excitement pulse contributing only insignificantly. This statement was checked by hitting the glass vial again during the recording period.

In order to eliminate further resonance frequencies stemming from the glass container, we divide the data by those obtained from a similar vial filled with methanol to the corresponding height. We note that at low frequencies only contributions from the mains frequency and the oscilloscope cooling fan were noticeable, the latter one with comparably small amplitude.

Data evaluation

The result of the procedure as described is shown in Fig. 1 and Fig. 2 as a thick solid curve. Many individual resonances can be observed with varying strengths. We here concentrate on the frequency position only.

The thin vertical lines represent the expected resonance frequencies for a cylindrical sample. These can be calculated from the wave equation in cylindrical coordinates r, θ, z , using a separation ansatz for these coordinates. The well-known solution leads to natural frequencies with wave vectors:

$$k^2 = \frac{\omega^2}{c^2} = k_{r,0}^2 + k_z^2 \quad (4)$$

which can be specified applying the appropriate boundary conditions. For acoustically hard walls, which require a wave node on the surface of the cylinder of height H and radius R , we obtain:

$$f = \frac{c}{2} \left[\left(\frac{u_{l,m}}{\pi R} \right)^2 + \left(\frac{n}{2H} \right)^2 \right]^{1/2} \quad (5)$$

where $\omega = 2\pi f$ has been used; $n = 2, 4, 6 \dots$ $u_{l,m}$ is the m -th root of the Bessel function of order l , which can be found, for example, in Abramowitz and Stegun [10].

In our case, the glass walls, to which the gel properly sticks, can be well approximated by hard walls. The gel-air surface, however, may be regarded as acoustically soft. In this case, we would have a node at the bottom of the glass vial and a crest at the surface. Accordingly, the lowest mode in z -direction exhibited a quarter wavelength instead of a half. The corresponding boundary conditions would lead to Eq. (5) with $n = 1, 3, 5 \dots$

Our experimental results, however, show that we need both contributions, i.e., we observe all modes with $n = 1, 2, 3, 4, 5, 6 \dots$ We interpret this observation in terms of a reflection coefficient (of intensity) that does not equal 1. Indeed, using a sound velocity of 4 m/s we obtain a reflection coefficient of approximately 0.6. We note, however, that shear waves do not propagate in isotropic bodies like fluids, implying a reflection coefficient of 1. This apparent contradiction cannot be resolved at present.

Results and discussion

Figure 1 shows exemplarily the results for a gel sample with nominal porosity $\phi = 97.5\%$. The thick curve is the experimental result, whereas the vertical thin lines

represent the calculations of the natural frequencies as described above. For clarity, only resonances with $l = 0$ are shown. The inner diameter of the glass vials, $2R = 27$ mm, and the height of the gel within the vial, $H = 27$ mm, have been determined independently. The sound velocity is then chosen such that the first calculated resonance fits the first experimental peak. A subsequent fine-tuning of c_T and the sample dimensions is performed for an optimal fit of all the resonances. We note that the gel meniscus and the vial bottom are slightly curved and the vial dimensions are not specified very accurately. We observe a very close agreement between experimental and calculated frequency positions, though the peak at $f = 175$ Hz is not present in the calculation. Note that the lowest resonance for $l = 1$ is expected at $f = 196$ Hz. From Fig. 1, we determine a sound velocity of $c_T = 4.1$ m/s.

Figure 2 shows the experimental result for the same gel, but with different sample dimensions; the glass vial has been simply filled with a smaller amount of liquid. The fitted sound velocity is $c_T = 4.2$ m/s, in close agreement with the previous one. However, it is clearly visible that the agreement between experimental data and calculated resonance positions is not as good as before. We regard this as an estimate for possible systematic sources of error in the determination of the sound velocity.

It remains to show that the determined sound velocity is due to the shear mode as claimed above. To do so, we have to determine the shear modulus and the density of our samples as a function of porosity independently.

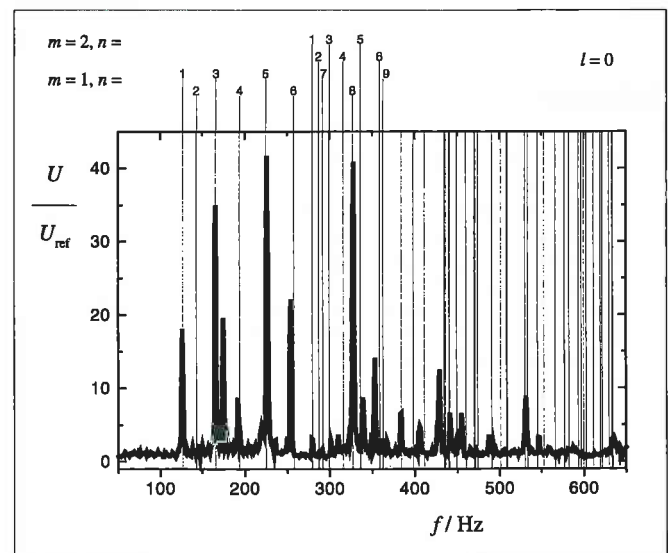


Fig. 1 Normalized sound amplitude as a function of frequency for a typical gel sample, $\phi = 97.5\%$. The sample dimensions, as obtained from the fit, are $H = 27$ mm, $2R = 26$ mm. The sound velocity is $c_T = 4.1$ m/s. Indices $l = 0, m, n$ are indicated for a few modes

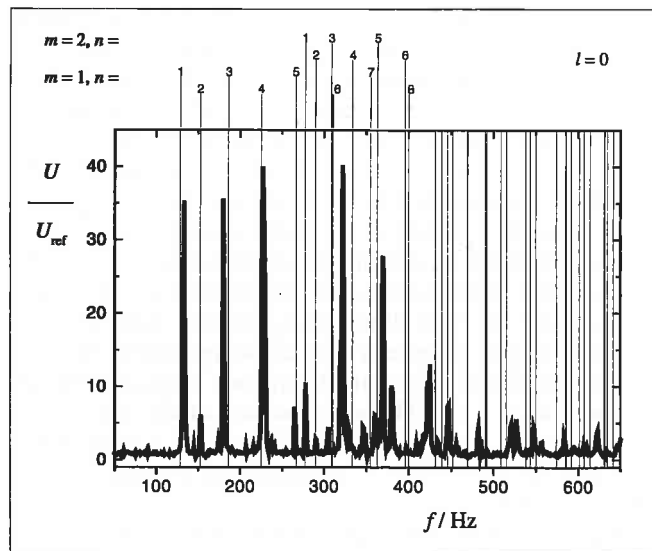


Fig. 2 Normalized sound amplitude as a function of frequency of the same gel as in Fig. 1, but with different sample dimensions: $H = 22$ mm, $2R = 27$ mm. The sound velocity is $c_T = 4.2$ m/s. Indices $l = 0, m, n$ are indicated for a few modes

These data can then be used to prove that Eq. (3) quantitatively describes the sound velocity as measured with the method introduced here. This will be demonstrated in a future publication. For this contribution, we restrict ourselves to numerical evidence.

The value of c_0 can be calculated according to Eq. (1) using $\phi = 0.975$, $\rho_f = 800$ kg/m³, $\rho_s = 2000$ kg/m³, $K_s = 30$ GPa, and $K_f = 0.71$ GPa. The moduli have been calculated from experimental sound velocity data

and the density of the bulk materials [5]. With these data we obtain $c_0 \approx 940$ m/s, a value which is clearly incompatible with the result of our measurements. A quick calculation shows that the ξ_i do not alter this statement.

On the other hand, if we use Eq. (3) for the calculation of the shear modulus of our sample, we obtain $G = 14$ kPa. This value seems to be reasonable in view of the data of Forest et al. [5], where the porosity was significantly lower ($\phi \approx 90\%$) than in the present study. In addition, they report a longitudinal sound velocity of the order of magnitude of c_0 as calculated above.

These calculations are a clear evidence for the statement that the "ringing gel" effect is connected to shear waves propagating in the porous material. In addition, Biot's theory is obviously applicable to the systems under study, though a rigorous proof requires the quantitative prediction of the sound velocity from macroscopic data, as mentioned above.

The results presented in this contribution allow a deeper insight into the nature of the "ringing gel" effect, which is an immediately noticeable and striking property of these soft materials. With some restrictions, one might even think of assembling a jelly xylophone from these materials, as the porosity of the samples can be varied easily.

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