Mechanical Strength of Amorphous $CaCO_3$ Colloidal Spheres

Michael Faatz, Wei Cheng, and Gerhard Wegner*

Max Planck Institute for Polymer Research, P.O.Box 3148, 55128 Mainz, Germany

George Fytas,† Raluca S. Penciu, and Eleftherios N. Economou

F.O.R.T.H/Institute of Electronic Structure and Laser, P.O. Box 1527, 71110 Heraklion, Greece, and Departments of Materials Science/Technology and of Physics, University of Crete

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Amorphous glassy $CaCO_3$ colloidal spheres of monomodal size distribution were studied by high-resolution Brillouin light scattering. The Young modulus of 37 GPa and shear modulus of 14 GPa of glassy $CaCO_3$ at a density of 1.9 g/cm^3 were extracted from the particle vibration frequencies by employing acoustic wave scattering cross-section calculations. The line shape of the low-frequency modes is a sensitive index of the particle polydispersity.

Brillouin spectroscopy resolves the light scattered inelastically by phonons propagating in a medium in the gigahertz frequency range. In homogeneous systems, the scattering wave vector of the photon, q, and the phonon, k, are equal and the observed Doppler frequency shift is $\omega = \pm ck$ where c is the speed of sound with longitudinal or transverse polarization. Hence, the elastic (at high frequency) moduli of the material, being equal to ρc^2 where ρ is the mass density, can be determined. For inhomogeneous media over length scales of the order of q^{-1}, the Brillouin spectrum $I(q,\omega)$ reveals rich spectral features[1−4] beyond the single doublet peak at $\pm cq$ corresponding to the effective medium. For isolated colloidal spheres, Brillouin spectroscopy (BS) can resolve localized (q-independent) modes associated with sphere vibrations[1,5,6] whose frequencies depend on the elastic properties of the particles and scale as $1/d$. Moreover, the spectral shape for the low-frequency eigenmodes depends on the particle size distribution, as was recently shown in the case of soft opals. Particle vibrational motion was, for the first time, revealed by Raman scattering[7,8] from nanoscopic crystallites.

Amorphous $CaCO_3$ has been identified as a precursor to its crystalline modifications calcite, vaterite, and aragonite in biomineralization.[9−11] Even some life forms have been found which preserve glassy $CaCO_3$ as part of their skeleton.[11] Little is known about the physical properties of amorphous $CaCO_3$ since a reproducible synthesis that produces a regular particle shape became available only very recently. This synthesis in which dialkyl carbonate in dilute aqueous solution serves as a source of CO_2 that is homogeneously formed in the medium produces spherical particles (droplets) of amorphous $CaCO_3$ of monomodal size distributions with diameters in the range between 400 and 1000 nm.[12] The precise diameter is subject to control parameters such as temperature of formation, rate of CO_2 production, and whether surfactants are added to stabilize droplets of smaller size. Amorphous $CaCO_3$ as produced exists in a metastable glassy state and contains water. The approximate composition as obtained from reaction is $CaCO_3{\cdot}0.5H_2O$. Residual water can be removed by careful drying, and water-free glassy $CaCO_3$ particles in the form of colloidal powders are obtained that are stable against recrystallization up to temperatures around 280 °C. At this temperature, calcite starts to be formed.

$CaCO_3$ powders obtained from calcite play an important role as fillers and modifiers in poly(olefine) composites and in pharmaceutical preparations. One could imagine that amorphous $CaCO_3$ that is easily synthesized directly in a monomodal particle size distribution could become an important material in these areas of application. The mechanical properties that are accessible by Brillouin spectroscopy are of primary interest. In the following, we report for the first time on these properties for colloidal $CaCO_3{\cdot}0.5H_2O$ prepared as reported in ref 12.

Freshly prepared powder of $CaCO_3$ particles was dispersed on a glass slide to form a thin white layer of colloidal spheres, as shown in the SEM image of Figure 1a. Images of this type allow estimating the particle size distribution displayed in Figure 1b. Due to strong multiple light scattering, only localized (q-independent) modes can be observed in the Brillouin (inelastic) spectra recorded either in a transmission (at a scattering angle of 15°) and or reflection configuration at 150° using a six-pass tandem

* To whom all correspondence should be addressed. E-mail: wegner@mpip-mainz.mpg.de.

† G. Fytas holds a joint appointment with MPI-P, Mainz.

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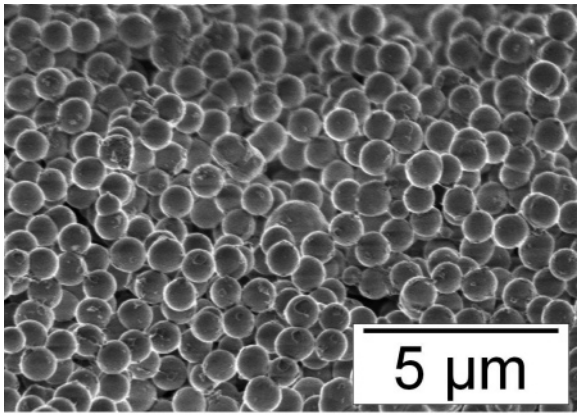

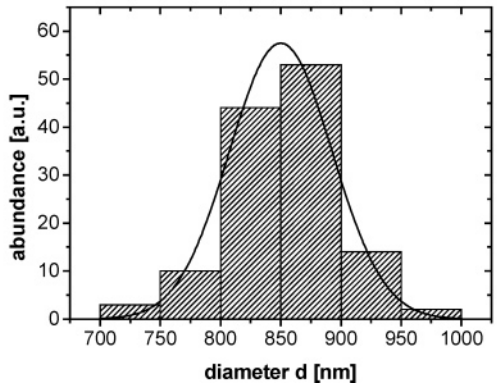

Figure 1. SEM image of the sample used for Brillouin spectroscopy (above) and particle size distribution from image analysis with a Gauss-curve fitting the polydispersity of the particle diameter d ($2w$ = 85 nm).

Fabry−Perot interferometer (FPI), and the experimental setup is described elsewhere.[1] Briefly, a solid-state Nd:YAG laser (532 nm) operating at 60 mW output power together with the incident beam optics were mounted on the arm of a goniometer to allow the variation of the scattering angle and hence q. The scattered light after passing FPI was detected by an avalanche photodiode connected with a multichannel analyzer. The spectrum $I(q,\omega)$ for each sample was recorded at two free spectral ranges (7.5 and 25 GHz) in order to achieve both high resolution and broad frequency range. Typical accumulation time for each spectrum was 5−10 h. The necessary stabilization of FPI was maintained over days using a reference beam during the scanning about the central Rayleigh line by means of a synchronized shutter blocking also the strong elastic ($\omega = 0$) scattered light from the film. A typical Brillouin spectrum recorded with 25 GHz free spectral range with a finesse of about 70 is shown in Figure 2 for $CaCO_3$ spheres with an average diameter d = 850 nm. To record as many eigenmodes as possible, the spectrum was also recorded at a higher resolution, indicated by the frequency range of the spectrum in the inset of Figure 2.

Several Brillouin doublets around the central (elastic) Rayleigh line are clearly resolved despite the small compressibility of the material compared to soft polymer-based colloidal particles.[6] The fact that these individual phonons can be resolved in the presence of strong multiple acoustic scattering identifies these signals as localized (q-independent) particle vibration eigenmodes.[6] Since the length scale of these modes usually matches the diameter, d, or the circumference of the spherical particle, their frequencies scale with $1/d$ as shown in Figure 3 for four

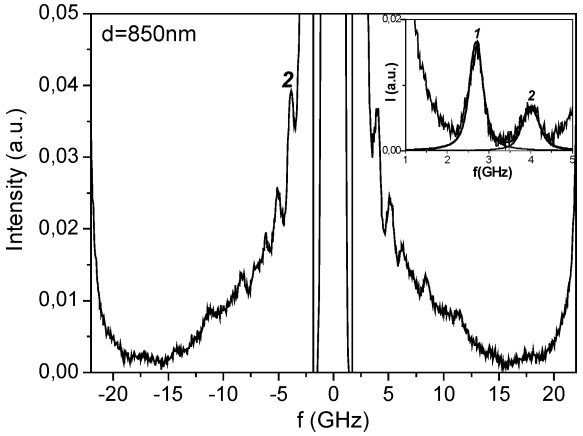

Figure 2. Inelastic light scattering (Brillouin) spectrum of a $CaCO_3$ colloidal particles with d = 850 nm spread on a glass slide recorded at two different resolutions: 25 and 7.5 GHz for the spectra in the main plot and the inset. The line shape of the two lowest-frequency modes (1,2) are described by convoluting a Gaussian particle size distribution with a Lorentzian natural line shape. Mode 1 is buried in the elastic Rayleigh line at low resolution (25 GHz) which resolves mode 2 and higher-frequency modes.

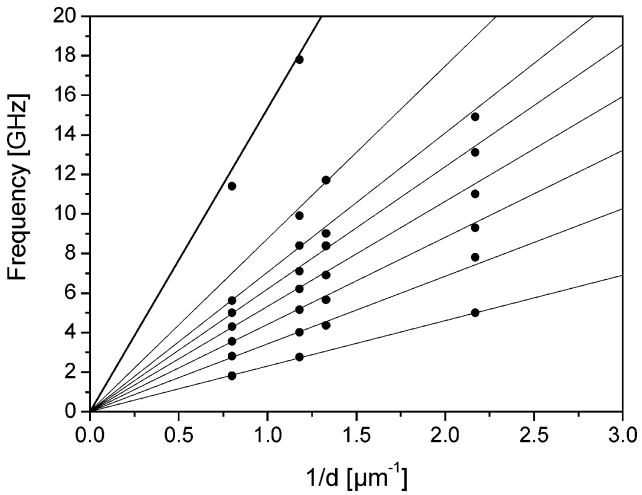

Figure 3. The frequency of vibration eigenmodes of the amorphous $CaCO_3$ particles plotted vs the inverse diameter. The solid lines represent the theoretical slopes ($f^*(i,l)$) of Table 1.

different samples of $CaCO_3$ spheres. As expected, the number of observed eigenfrequencies increases with d.

The eigenfrequencies, denoted by $\omega(i, l)$ for the i-th mode of the l-th harmonic, of an elastic sphere oscillations in a vacuum can be separated in two groups: The first is associated with the so-called toroidal oscillations which are purely transverse; these eigenfrequencies are given by the roots of the equation $(l - 1)\, j_l(x_T) - x_T\, j_{l+1}(x_T) = 0$, where $x_T = \omega(i, l)d/2c_T$, with c_T being the transverse sound velocity and j_l are spherical Bessel functions.[13] Because of the purely transverse nature of these eigenmodes, we do not expect this type of oscillation to be excited appreciably by the laser light. The other group is of mixed longitudinal and transverse character and are called spheroidal oscillations; their eigenfrequencies are given by the roots of a 2 × 2 determinant whose b_{ij} (i,j = 1,2) elements are functions involving spherical Bessel functions of x_T and $x_L = \omega(i,l)d/2c_L$, where c_L is the longitudinal sound velocity. It is more instructive to find $\omega(i,l)$ for the

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Table 1. Comparison between Experimental and Computed $CaCO_3$ Particle Eigenfrequencies $f^* = fd$[a]

index	eigenfrequencies	$f^*(i,l) = f(i,l)d$ (nm GHz)
(i,l)	computed	experimental
(1, 2)	2299	2310 ± 50
(1, 3)	3422	3550 ± 110
(1, 4)	4402	4270 ± 180
(1, 5)	5312	5060 ± 200
(1, 6)	6185	6050 ± 240
(1, 7)	7041	6850 ± 300
(1, 9)	8734	8640 ± 350
(1, 17)	15 347	14 960 ± 600
(1, 20)	17 807	17 920
(2, 24)	21 016	21 430

[a] The theoretical calculations are based on the resonances in an acoustic wave scattering cross-section by a single $CaCO_3$ spherical particle ($\rho = 1.9$ g/cm^3, $c_L = 5.6$ km/s, $c_T = 2.7$ km/s) in air. The pair of numbers (i,l) referring to the i-th mode of the l-th harmonic identify the vibration modes observed experimentally (see Figure 3).

spheroidal oscillations as sharp peaks (resonances) in the cross-section of a plane acoustic wave scattered by a single $CaCO_3$ particle; the strength of each resonance provides some indication regarding its excitation by light. To obtain explicit results for the eigenfrequencies, we need the values of d, c_L, c_T, and ρ; d is obtained as input parameter from SEM (Figure 1) and c_L from the longitudinal Brillouin phonon frequency, ω_L. In the presence of strong multiple light scattering, ω_L is the cutoff frequency (spectrum not shown) corresponding to the phonon with the q of the backscattering (180°) geometry.[6] In $CaCO_3$, c_L amounts to (5.6 ± 0.2) km/s. The calculations were then run with two floating parameters: ρ and c_T. By choosing $\rho = 1.9$ g/cm^3 and $c_T = (2.7 \pm 0.1)$ km/s, we obtained the computed values shown in Table 1, which are compared with experimentally observed eigenfrequencies represented in the reduced form $f^*(i,l) = f(i,l)d$, where $f(i,l) = \omega(i,l)/2\pi$. The agreement is very good for all 10 experimental eigenfrequencies, which allows us to have confidence in the so-determined values of c_T and ρ.

The Poisson ratio $\sigma = (c^2_L - 2c^2_T)/[2(c^2_L - c^2_T)]$ amounts to 0.35 (∼1/3). The fact that one transverse sound velocity suffices to reproduce all observed eigenfrequencies is strong support of the amorphous state of the $CaCO_3$ spheres in agreement with the X-ray scattering data.[12] For the crystalline $CaCO_3$ (calcite), the reported values are 7.4 km/s for the bulk and 2.9 and 4.4 km/s for the two transverse sound velocities.[14]

To a first approximation, c_L can be related to the Young modulus and c_T to the shear modulus of the material. The Young modulus is given by $E = c_L^2\rho(1 + \sigma)(1 - 2\sigma)/(1 - \sigma) = 37$ GPa, which is comparable but lower (as expected) than the range of moduli found for common inorganic glasses (60−150 GPa)[15] and it is about 1 order of magnitude larger than the commonly found values for glassy polymers (3−5 GPa).[16] On the other hand,the shear modulus (ρc^2_T) assumes the value of 14 GPa. We note that a value for the density of amorphous $CaCO_3$ of 1.9 g/cm^3 was also found by Ballauff et al.[17] recently. These authors used a totally different method of preparation that depended on surfactants present in the precipitation process.

Taking into account the $1/d$ scaling of $f(i,l)$, a Lorentzian natural shape of the resonance, and a Gaussian distribution of the particle diameter x, $P(x) = (w\sqrt{2\pi})^{-1} \exp[-(x - d)^2/2w^2]$, we have fitted (solid lines in the inset of Figure 2) the observed broad line shape of the modes (1,2) and (1,3) with the same value of $2w = 70$ using the formula,[6]

$$I(\omega) = \int \mathrm{d}x P(x)\{\Gamma(x)/[(\omega - \omega(x))^2 + \Gamma^2(x)]\} \quad (1)$$

where $\omega(x) = 2\pi f^*(i,l)/x$ and $f^*(i,l)$ are the experimental values (Table 1) for the eigenfrequencies (1,2) and (1,3).The natural half width at half-maximum, $\Gamma(x)$, is close to the instrumental width for monodisperse particles without internal (relaxation) losses such as the present glassy $CaCO_3$. It is the higher value of $f^*(1,3)$ which makes the line shape of the (1,3) mode broader than that of (1,2) at constant size polydispersity. Note that the variance obtained from image analysis (cf. Figure 1) coincides reasonably well with the one extracted from the line shape of the Brillouin eigenmodes.

In summary, Brillouin light scattering from nontransparent films of colloidal amorphous $CaCO_3$ spheres yields the values of the two mechanical moduli at gigahertz frequencies, as well as their size distribution. Since the inelastic light scattering spectrum of the individual spheres is unique, their agglomeration in irregular clusters seriously affects the fine structure of the experimental spectra.

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