

## Sound Propagation in Suspensions of Colloidal Spheres with Viscous Coupling

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We measure attenuation and phase velocity of sound waves in suspensions of colloidal silica spheres. As the concentration of colloids increases, the dependence of the attenuation changes from linear to at least quadratic in volume fraction. This change is attributed to a viscous coupling of neighboring scatterers. When the wavelength is comparable to the sphere size, the sound velocity decreases with increasing volume fraction and falls below that of the pure liquid. [S0031-9007(99)08508-7]

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Propagation of acoustic and electromagnetic waves in inhomogeneous media is a phenomenon of great fundamental importance and increasing technological relevance. In the case of strong multiple scattering, intriguing effects such as band formation or wave localization are expected to occur as a result of interference [1]. These exciting predictions have stimulated experimental research, largely focused on the electromagnetic case, for many years. Anderson localization of light has recently indeed been observed [2]. By contrast, to date only a few experiments on sound propagation in the strongly scattering regime have been performed [3–6]. However, these experiments yielded astonishing results. Liu *et al.* [3], for example, studied phonon dispersion curves in colloidal suspensions and found, contrary to a pure liquid, two longitudinal propagating modes. These authors also report gaps in the dispersion relation.

One of the parameters that play a decisive role is the ratio of the sound wavelength to the size of scatterers. In general, the scattering cross section depends strongly on this ratio. Another important length scale that can profoundly influence acoustic propagation is the viscous penetration depth  $\delta$  ( $\delta = \sqrt{2\eta/\rho\omega}$ , with  $\eta$  being the shear viscosity,  $\rho$  the density, and  $\omega$  the angular frequency). If transverse or vortex modes are excited in a liquid, their amplitude decays exponentially with decay length  $\delta$ . For long wavelength sound propagation the viscous depth can be of great importance. In liquid saturated porous media, for instance, propagating modes can become diffusive and vice versa, depending on the ratio of the viscous length to the pore size [7]. Recent acoustic band structure calculations predict similar effects for suspensions of isolated spherical scatterers, where the interparticle separation plays the role of the pore size [8]. If  $\delta$  is larger than the interparticle separation, scatterers are coupled by viscous forces. Despite the importance of  $\delta$ , there are to date no experiments addressing possible effects of viscous coupling in the regime where the sound wavelength becomes comparable to the inhomogeneity length scales.

In this paper, we report the first investigation of acoustic wave propagation in strongly scattering media with vis-

cously coupled scatterers. Brillouin spectroscopy is used to measure sound attenuation and velocity dispersion in suspensions of colloidal silica spheres. The viscous penetration depth is of the order of the sphere radius in the frequency range investigated. The separation between the surfaces of the spheres,  $l_{\text{free}}$ , is varied by changing the solid volume fraction  $\phi$ . We are thus able to perform measurements in the two regimes  $\delta < l_{\text{free}}$  (no viscous coupling) and  $\delta \geq l_{\text{free}}$  (viscous coupling). This is in contrast to previous studies [3–6]. We find that, in the absence of viscous coupling, the sound attenuation increases linearly with volume fraction, as expected. To our surprise, the attenuation increases at least quadratically with  $\phi$  in the case  $\delta \geq l_{\text{free}}$ . However, the absolute values of the attenuation for  $\delta \geq l_{\text{free}}$  are, at not too large volume fractions, smaller than expected from the low- $\phi$  results. These or similar effects have not, to our knowledge, been reported before. The sound velocity  $v$  decreases with increasing volume fraction when the wavelength is comparable to the sphere size. Viscous coupling has no effect on  $v$ .

Monodisperse colloidal silica spheres with radius  $r = 59$  nm are suspended in an optically index matching mixture of ethanol and benzyl alcohol. The colloid volume fraction is controlled by centrifuging the initial suspension and removing the liquid on top of the sediment. Then, known amounts of liquid are added stepwise and the particles resuspended. The colloid concentration  $c$  is determined by drying a known volume of the last suspension in the series and weighing the residue; the range is  $0 \leq c \leq 1.188$  g/cm<sup>3</sup>. The density of our colloidal silica is about 2 g/cm<sup>3</sup>, giving  $0 \leq \phi \leq 0.59$  for the volume fraction.

The colloids are slightly charged if dispersed in a liquid and interact by a screened repulsive coulomb potential, inhibiting aggregation. As a result, the diffusion of the colloids “freezes” at volume fractions of about 35%. The freezing transition is detected by the appearance of a long time tail in the intensity autocorrelation function of residual light scattered from the particles, which we measure by dynamic light scattering. In the following, we will refer to the low- $\phi$  phase of the colloids, where the particles diffuse freely, as the “fluid phase.” The high- $\phi$

state, where diffusion is absent, will be referred to as the “solid phase.” These terms should not be confused with the “liquid” and the “solid,” meaning the suspending medium and the colloidal particles themselves, respectively. Another possibility to stabilize colloidal suspensions is the coating of the particles with a thin polymer layer. However, the acoustic properties of a polymer layer on the sphere surface are unknown and, consequently, the solid-liquid interface becomes ill defined. More importantly, a polymer layer would prevent the particle surfaces from approaching to distances much smaller than the viscous depth.

Concerning the acoustic parameters, the suspensions are strongly inhomogeneous on the length scale of the particle radius. The density ratio  $\rho_{\text{solid}}/\rho_{\text{liquid}}$  is about 2 and the (longitudinal) velocity contrast  $v_{\text{solid}}/v_{\text{liquid}}$  is about 4. The ratio of the transverse sound velocity in the solid to the longitudinal velocity in the liquid is about 2.6. This acoustic mismatch is substantially larger than in earlier experiments [3].

The viscosity of the suspending alcohol mixture is 2.77 mPa s. Brillouin measurements are performed in the range  $0.72 \leq qr \leq 2.04$ , where  $q$  is the sound wave vector. In the corresponding frequency range, we have  $11 \leq \delta \leq 18$  nm. For  $\phi \geq 0.37$  the average penetration depth  $\langle \delta \rangle = 14.5$  nm is larger than the average separation between the sphere surfaces ( $l_{\text{free}} = N^{-1/3} - 2r$ , where  $N = 3\phi/4\pi r^3$  is the number density of scatterers), such that viscous coupling of spheres occurs.

Brillouin spectra are obtained using an argon ion laser at  $\lambda = 514.5$  nm. The scattered light is imaged onto a 200- $\mu\text{m}$  pinhole and collimated into a Fabry-Perot interferometer (free spectral range 18.2 GHz), operated in triple-pass configuration. The sound wave vector is selected by changing the scattering angle  $\theta$ . The phase velocity is obtained from the center frequency  $\omega(q) = vq$  of the Brillouin peaks, and the attenuation coefficient  $\xi$  from the full width at half maximum  $\Delta\omega$ .

Figure 1 shows typical Brillouin spectra at different volume fractions. We observe one propagating sound mode for all concentrations of colloids and wave vectors. Whereas the center frequency of the peaks changes only weakly with increasing volume fraction, the width increases strongly and eventually becomes of the same order as the center frequency.

The sound dispersion relation  $\omega(q)$  is shown in Fig. 2 for two different volume fractions. At the lowest volume fraction we obtain a straight line, as in the pure liquid. At larger volume fractions the sound velocity becomes dependent on the wave vector, thus depressing the dispersion relation at large  $q$ . This depression becomes continuously larger as the volume fraction is increased. As a result, the dependence of the sound velocity on volume fraction at large wavelengths (or small  $q$ ) is qualitatively different from that at small wavelengths (or large  $q$ ), as is evident from Fig. 3. It shows the sound velocity, normal-

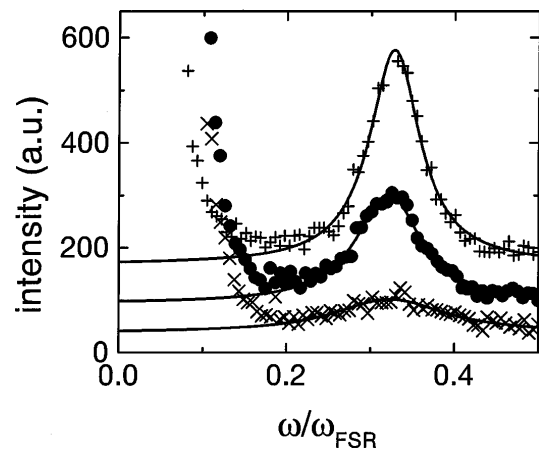


FIG. 1. Rayleigh-Brillouin spectra at  $\theta = 90^\circ$  for three volume fractions of colloidal silica spheres in an optically index matching alcohol mixture. Volume fractions are  $\phi = 0.074$  (+), 0.23 (•), and 0.46 (×). The lines are Lorentzian fits to the data.

ized by that of the pure liquid, as a function of  $\phi$ . Data at two representative wave vectors, obtained from the dispersion curves (Fig. 2), are presented. At large wavelengths, the sound velocity increases with increasing volume fraction and becomes larger than that in the pure liquid. This increase is expected for the composite medium, since the sound velocity in the colloidal spheres is much larger than that in the liquid. At small wavelengths, the behavior becomes completely different: Here, the sound velocity *decreases* with increasing volume fraction, despite the fact that the amount of high velocity material increases. The sound velocity even falls below that of the pure liquid. Such slow propagation velocities have also been observed in ultrasonic experiments on macroscopic glass spheres in

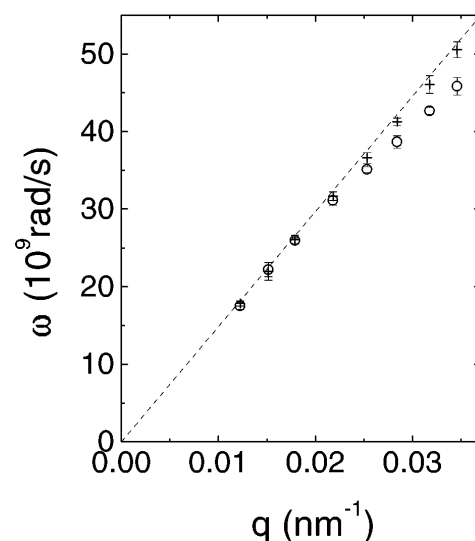


FIG. 2. Sound dispersion relation for colloidal suspensions with volume fractions  $\phi = 0.074$  (+) and 0.28 (o). The dashed line represents the long wavelength limit for  $\phi = 0.28$ .

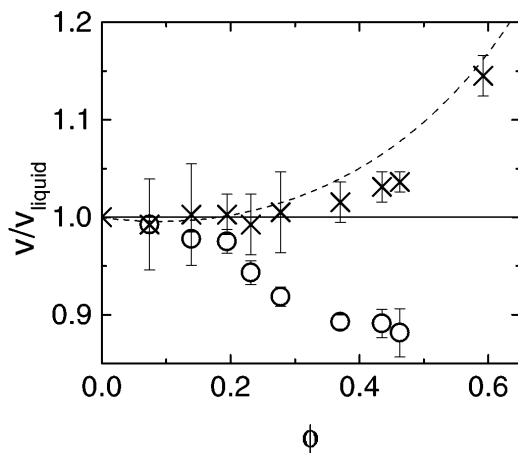


FIG. 3. Phase velocity of the high frequency sound mode in suspensions of silica colloids as a function of colloid volume fraction. The velocity is shown for two representative wave vectors:  $qr = 0.89$  ( $\times$ ) and  $1.87$  ( $\circ$ ). The data are normalized by the sound velocity in the pure liquid. The dashed line represents the long wavelength limit. No spectrum could be obtained for the largest volume fraction at  $qr = 1.87$  due to overdamping of the sound mode.

water [4] and can be understood in terms of multiple scattering theory [9,10]. Most of the wave energy at large  $q$  is confined to the liquid because of the large acoustic contrast (and  $v_{\text{liquid}} < v_{\text{solid}}$ ); as a result, the propagation velocity is close to that of the pure liquid [10].

As mentioned above, the average viscous penetration depth is larger than the separation between sphere surfaces for  $\phi \geq 0.37$ . This viscous coupling does not have a noticeable influence on the velocity.

The sound velocity shows a modest, but significant, dependence on wavelength and volume fraction. The attenuation, however, will show a much stronger dependence, as the quantities governing wave propagation enter more directly. Damping effects are described by the extinction mean free path  $l_{\text{ext}}$ , which is related to the extinction cross section  $\sigma_{\text{ext}}$  by  $1/l_{\text{ext}} = N\sigma_{\text{ext}} + 1/l_0$  [11]. The extinction cross section contains the scattering cross section and possibly a contribution due to friction at the solid-liquid interface. The term  $1/l_0$  denotes absorption due to the pure liquid. If  $\sigma_{\text{ext}}$  is independent of  $N$ , one expects a linear increase of the attenuation with increasing concentration of scatterers. The width of the Brillouin peaks is related to the extinction mean free path by  $\Delta\omega = v/l_{\text{ext}}$ , since the intensity of the sound wave in a given direction decays exponentially with decay length  $l_{\text{ext}}$ .

Figure 4 shows  $\Delta\omega$  as a function of squared wave vector for three volume fractions. In a pure liquid, the width is related to losses by diffusive processes, which leads to a  $q^2$  dependence [12]. In the colloidal suspensions considered here, we also observe  $\Delta\omega = \xi q^2$  in the  $q$  range investigated. However, in this case the  $q^2$  dependence, seen at all volume fractions, is to a large extent due to the scattering cross section of a single

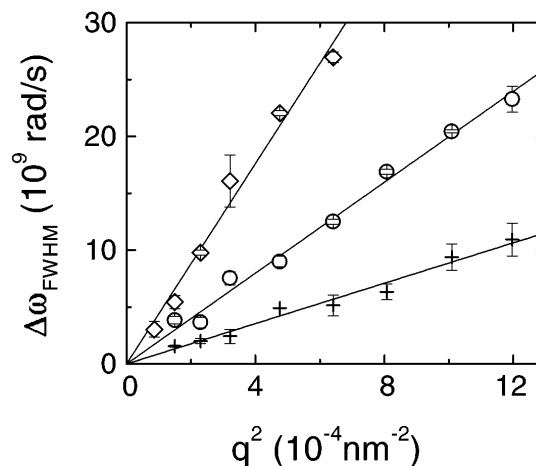


FIG. 4. Full width at half maximum of Brillouin peaks versus squared wave vector. Data for three volume fractions of silica colloids are shown:  $\phi = 0.074$  ( $+$ ),  $0.28$  ( $\circ$ ), and  $0.59$  ( $\diamond$ ). The straight lines are fits to the data.

sphere [10]. The attenuation coefficient  $\xi$  increases by almost 1 order of magnitude from the pure liquid to the most concentrated sample, showing that the presence of inhomogeneities strongly affects wave propagation. In order to focus on this  $\phi$  dependence, we plot  $\xi$  as a function of volume fraction in Fig. 5. For a proper

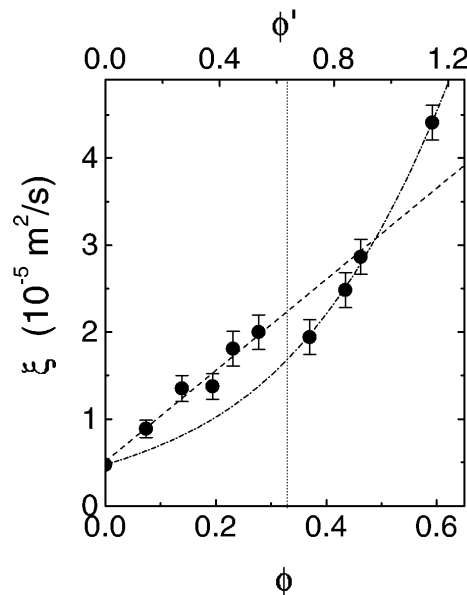


FIG. 5. Sound attenuation coefficient  $\xi = \Delta\omega_{\text{FWHM}}/q^2$  for the sound mode in suspensions of colloidal silica spheres versus colloid volume fraction. The dashed line is a fit to the points for  $0.074 \leq \phi \leq 0.28$ . The dash-dotted line is a guide to the eye. The suspensions are in a fluid phase at  $\phi \leq 28$  vol%, whereas the colloid diffusion is frozen in at the larger volume fractions; the corresponding branches are treated separately. It is seen that the points at low volume fractions lie on a straight line through  $\xi(\phi = 0)$ , whereas the points at high volume fractions do not.  $\phi'$  is obtained from  $\phi$  by replacing  $r$  with  $r + \langle\delta\rangle$ . The dotted line represents  $\phi' = 0.64$ .

analysis of the volume fraction dependence, the points taken in the colloidal fluid phase ( $\phi \leq 0.28$ ) must be treated independently from those in the solid phase ( $\phi \geq 0.37$ ). Strikingly, the attenuation coefficient manifests a change in concentration dependence at about  $\phi = 0.3$ : Whereas  $\xi$  increases linearly with concentration at small  $\phi$  (“fluid phase branch”), as expected for independent scattering, the increase is at least quadratic at large volume fractions (“solid phase branch”).

Contrary to the sound velocity, viscous effects are evident in the attenuation. It is known from the long wavelength limit that viscosity leads to an enhancement of the scattering cross section, if  $\delta$  is not negligible with respect to  $r$  [12]. We observe a similar effect here. To demonstrate this, we replace the “bare” radius  $r$  by  $r' = r + \langle \delta \rangle$ . The cross section depends on the radius via the size parameter  $qr$  and the geometric cross section  $\pi r^2$ ; in our case, we have  $\sigma/\pi r^2 \propto (qr)^2$ . With the transformation  $r \rightarrow r'$  the cross section, derived from the straight line in Fig. 5 according to  $1/l_{\text{ext}} = N\sigma_{\text{ext}} + 1/l_0$ , is in reasonable quantitative agreement with a calculation of the scattering cross section for a comparable system (a glass sphere in water) in the regime  $\delta \ll r$  [10]. Obviously, this description in terms of scattering by independent scattering units with radius  $r'$  is only valid as long as the scattering units do not overlap; in the case of overlap, the total volume occupied by the scattering units is smaller than the sum of the individual volumes, which will lead to a reduction of the damping as compared to the case of nonoverlapping scatterers. Indeed, the transition of the attenuation to the solid phase branch occurs if the renormalized volume fraction  $\phi'$  ( $\phi' = \phi r'^3/r^3$ ) approaches the value of random close packing, and the attenuation coefficient is at first smaller than expected from an extrapolation of the low- $\phi$  values. These observations corroborate our interpretation. Now, comparing the average viscous depth to the average separation between the sphere surfaces,  $l_{\text{free}}$ , we find that  $\langle \delta \rangle/l_{\text{free}} \approx 1$  at  $\phi = 0.37$ . At this volume fraction, the spheres become connected by viscous forces. Viscous coupling of spheres provides an energy transfer mechanism between neighboring scatterers through excitation of transverse modes that will depend at least quadratically on volume fraction. The energy transferred by viscous coupling will be seen as an effective loss in the sound mode observed, and thus as an increase in attenuation. We believe that this mechanism is responsible for the qualitative difference seen in the volume fraction dependence between the solid phase branch and the fluid phase branch. The quantitative importance of viscous coupling may be sensitive to the degree of order in the solid phase. On the basis of these

measurements, however, possible structural effects cannot be quantified.

In conclusion, we have shown that strong scattering of sound waves leads to the counterintuitive effect that the propagation velocity decreases with an increasing amount of high velocity material. We have presented evidence that the parameter  $\delta/l_{\text{free}}$  is of great importance for the sound attenuation: In the regime of viscous coupling ( $\delta \geq l_{\text{free}}$ ), new effects have been observed.

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