PHONON DISPERSION IN SUSPENSIONS OF HARD SPHERE COLLOIDS*

D.A. WEITZ, J. LIU, L. YE AND PING SHENG
Exxon Research and Engineering Co., Rt 22E, Annandale, NJ 08801.

ABSTRACT

We use Brillouin scattering to measure the dispersion of the propagating acoustic modes in a suspension of hard sphere colloids. We find two distinct longitudinal modes when the sound wavelength becomes comparable to the sphere diameter. The higher frequency mode has a velocity intermediate between those of the pure solid and the pure liquid phases, and its velocity increases with increasing volume fraction, ϕ. The lower frequency mode has a velocity less than the velocities in either the pure fluid or pure solid phases, and its velocity decreases with increasing ϕ. We interpret the higher frequency mode as a compressional wave which propagates through both the solid and the fluid, as expected for a composite medium. The lower frequency mode has not been observed before, and is interpreted as a surface acoustic mode, which propagates between adjacent spheres through a decaying portion of the excitation in the fluid.

INTRODUCTION

The propagation of acoustic waves through a random, disordered material is one of the most fundamental properties that characterize the medium. This is particularly true of granular materials, where the structure and correlations between the grains can have a profound effect on the propagation of acoustic waves. One class of granular material whose acoustic properties have been widely studied is porous media, comprised of solid and fluid phases. Their acoustic properties are of immense practical importance because of their utility for seismic investigations and other non–intrusive probes; they are also of great fundamental interest because of the rich variety of fascinating phenomena that have been observed. The complex interplay between the acoustic frequency, sound wavelength and characteristic size of the microstructure, as well as the presence of large interfacial areas and the frequency dependence of the viscous coupling between the solid and the liquid, lead to new mechanisms for the propagation of acoustic waves in these materials.

The structure and connectivity of the solid grains play a critical role in determining the propagation of acoustic waves through these media. One of the simplest and most fundamental structures consists of uniform solid spheres immersed in a fluid.[1] The characteristics of this system are highly controllable, as the grain size, solid volume fraction, acoustic wavelength and acoustic frequency can all be independently varied. An example of such a structure is a hard sphere colloid.[2] This consists of a dispersion of monodisperse, solid spheres immersed in a fluid, interacting solely by the hard sphere repulsion due to the fact that two solid spheres can not occupy the same volume. In this paper, we present the results of a study of the acoustic propagation through a hard sphere colloid.[3] We report Brillouin scattering measurements of the thermally excited, propagating acoustic modes, and present the dispersion curve for longitudinal phonons in a hard sphere colloid. The behavior observed is surprising and unexpected. Since the continuous phase is a fluid which can not support shear, there is no long range rigidity in this medium. Thus, in the limit of long wavelength, it can be rigorously shown that the medium can support only one propagating longitudinal acoustic wave.[4] This behavior is widely expected to persist to shorter wavelengths.[1] In this paper, we show that this is not the case. As the sound wavelength becomes comparable to the sphere diameter, a new and unexpected mode appears which exhibits unusual behavior. We suggest that this new excitation is a coupled interface mode.

The hard sphere colloids used here consist of monodisperse polymethylmethacrylate (PMMA) spheres, sterically stabilized by a thin layer of grafted polymer, with a thickness

*This paper is dedicated to our friend and colleague, Ben Abeles, on the occasion of his 65th birthday. Throughout his career, Ben has been a leader both as a scientist and as a person, setting an example for all his colleagues to follow. We have all learned a great deal from Ben's love of science and of life. Keep climbing, Ben.

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of about 15 nm. The colloidal particles are immersed in an index–matching mixture of dodecane and carbon disulphide, eliminating multiple scattering, even at the highest volume fractions. This makes it possible to use light scattering techniques to study the structure and characteristics of these colloids, even though the particle size is comparable to the wavelength of light. These hard sphere colloids have been of great interest in their own right, as they exhibit a rich phase behavior that possesses strong analogies to that of a simple, hard sphere atomic system.[2] At low volume fractions, ϕ, the colloidal particles behave as a fluid, with short range correlations between the particles that are well characterized by a liquid like structure factor. For larger volume fractions, $\phi > 0.49$, the colloidal particles form either a colloidal glass or a colloidal crystal.

We use static light scattering to determine the structural correlations of the spheres by measuring the static structure factor, $S(q)$, where q is the scattering wavevector. We use Brillouin scattering to determine the frequency of the propagating sound modes by measuring the dynamic structure factor, $S(q,\omega)$. Brillouin scattering probes the thermally excited propagating longitudinal acoustic waves in the medium. A peak is observed in the Brillouin spectrum at a frequency corresponding to a propagating sound wave whose wavelength, λ, matches the inverse scattering wavevector. By varying q, we can vary the size of the acoustic wavelength relative to the sphere diameter, d, and we can measure the dispersion curves for the longitudinal phonons in the suspension of hard sphere colloids.

EXPERIMENTAL

The Brillouin scattering was performed using single–mode Ar^+ or Kr^+ lasers with wavelengths of 5145 Å or 6471 Å respectively. The spectra at a given q were found to be independent of the laser wavelength. The colloids exhibit rather strong self–focusing of the laser beam, which is considerably more pronounced in the green than in the red. Thus the power incident on the sample was kept below about 100 mW, focused to a beam of about 100 μm diameter. At all times, we ensured that the incident power was sufficiently low as to not affect the spectra. The scattered light was imaged onto a 150 μm diameter pinhole and then collimated into a Fabry–Perot interferometer. Despite the fact that the colloids were index matched, the elastically scattered light was still about four orders of magnitude more intense than the Brillouin peaks. Thus, to obtain sufficient rejection of the intense Raleigh peak, and to increase the resolution, the Fabry–Perot interferometer was operated in a five–pass configuration with a finesse of about 50.

We measure the velocity of the acoustic modes from the frequencies of the peaks in the Brillouin spectra, $v=\omega/q$. By varying the scattering angle, we can vary the scattering wavevector, q, enabling us to measure the dispersion relation for the longitudinal phonons. Our Brillouin measurements are made at scattering angles ranging from about 9° to 170°, corresponding to q varying from .003 to .04 nm^{-1}. Since we are interested in the properties of the acoustic propagation as the sound wavelength changes with respect to the sphere size, the dimensionless parameter of interest is qd. We extend the accessible range of qd by using spheres of different sizes. The first sample consists of spheres which have diameters of 370 nm, including the grafted polymer layer. The core diameter, consisting of solid PMMA, is then 340 nm, allowing data to be obtained for qd ranging from about 1 to 14. These spheres are most convenient for studying the behavior near the peak in the static structure factor, which occurs near $qd \approx 2\pi$. The second sample consists of spheres which have diameters of 680 nm, with core diameters of 650 nm, allowing data to be obtained for qd ranging from about 2 to 25. Thus, these spheres are most convenient for studying the behavior as qd becomes much larger than 2π.

In addition to varying qd, we also obtain data for different values of the volume fraction of the solids, ϕ. This is determined from their phase behavior.[2] The samples are gently centrifuged until the colloids sediment at the bottom of the containers. We assume that the sediment is comprised of randomly close packed spheres, with ϕ_e=0.64, and use this as the highest volume fraction studied. For the other samples, the heights of the sediment and the supernatent are measured and the volume fraction of colloids in the total suspension is calculated. The samples are then well mixed again before the Brillouin experiments are performed. This method provides a measure of the effective hard sphere volume fraction which determines the phase behavior of the colloids and includes the contribution of the thin layer of stabilizing polymer coating each sphere. The colloids themselves form a disconnected system of solid spheres, even at the highest volume

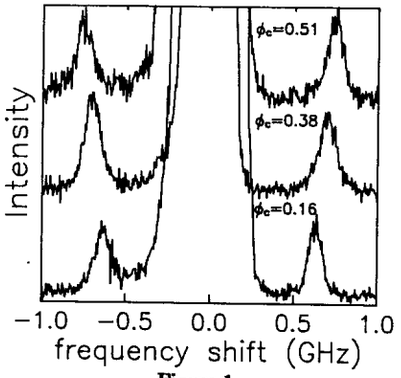


Figure 1.
Brillouin spectra for three different volume fractions of 370 nm diameter PMMA spheres measured at a q=0.0034 nm^{-1}, corresponding to qd=1.1, in the hydrodynamic regime for the propagation of acoustic waves.

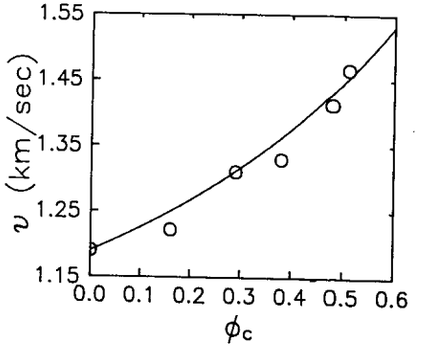


Figure 2.
The volume fraction dependence of the sound velocity measured at small angle, qd=1.1, in the hydrodynamic regime for the propagation of acoustic waves using the 370 nm diameter spheres. The solid line is the effective medium theory calculation using the measured values for the sound velocities in the pure phases. Much better agreement is obtained using the core volume fraction, ϕ_c, rather than the the effective volume fraction, ϕ_e.

fractions. We calculate the volume fraction of the solid PMMA, or the core volume fraction, ϕ_c, from ϕ_e by assuming that the grafted layer of stabilizing polymer has a thickness of 15 nm. We estimate the total uncertainties in the values determined for ϕ_c to be about ±5%, arising primarily from the errors introduced when measuring the heights. Thus the uncertainty is substantially less for the sample with the highest volume fraction, ϕ_e=0.64, where the uncertainty arises only in the knowledge of the precise thickness of the grafted polymer layer. Finally, we ensure that none of the samples are allowed to settle and form colloidal crystals, so that there is no long range order between the particles used to obtain the data reported in this manuscript.

RESULTS

In the limit of very low scattering angles, when the wavelength of the sound is much larger than the sphere size, we expect to observe hydrodynamic behavior, with only a single propagating sound mode. The lowest value of qd that we can achieve is $qd \approx 1$, using the smaller spheres. Brillouin spectra for three different volume fractions, ϕ_c=0.16, 0.38, and 0.51, are shown in Fig. 1. For the lowest volume fraction, ϕ_c=0.16, the Brillouin peak is almost unchanged in shape and position from that observed in the index matching fluid with no spheres present. However, the intensity of the Raleigh peak is increased by several orders of magnitude with the addition of the spheres, while the intensity of the Brillouin peak is virtually unchanged. As ϕ_c increases, the Brillouin peaks shift to larger frequencies and become broader. This behavior is expected, since the velocity of sound in the solid is roughly twice that in the fluid.

Since λ is substantially larger than d, the behavior can be well described using an effective medium model to account for the velocity of sound as a function of volume fraction. In Fig. 2, we plot the sound velocity determined from the frequency of the Brillouin peak, $v=\omega/q$, as a function of core volume fraction, ϕ_c. We compare the data to a theoretical prediction based on an effective–medium theory appropriate for isolated spheres immersed in a fluid.[5] We take the average velocity to be

$$v = \sqrt{\frac{\beta}{\rho}}$$

where the average elastic modulus is given by Wood's approximation,

$$\frac{1}{\beta} = \frac{\phi}{\beta_s} + \frac{1-\phi}{\beta_f}$$

and the average density is given by

$$\rho = \phi\rho_s + (1-\phi)\rho_f$$

where the subscripts s and f refer to the solid and fluid respectively. This expression for the elastic modulus is rigorously correct in the limit of long sound wavelength,[4] as is the case for these values of qd. All the parameters in these expressions are known. The elastic modulii of both the solid and the liquid phases are determined experimentally using Brillouin scattering from the pure materials. The density of the index-matching fluid is determined from the measured ratio of solvents used to index match the spheres, while for the PMMA, we use the bulk density. As shown by the solid line in Fig. 2, the agreement with the data is very good, confirming the hydrodynamic nature of the acoustic behavior in this region. Furthermore, much better agreement is obtained using the core volume fraction, ϕ_c, than using the effective hard sphere volume fraction determined from the phase behavior. This confirms that the grafted polymer layer behaves more like the fluid rather than the solid for sound propagation. Thus we use the core volume fraction and the core radius to characterize the spheres for all our measurements.

As q increases, a qualitative change is observed in the Brillouin spectra. This change is initially observed when q approaches 0.009 nm^{-1}, which corresponds to qd approaching π. Here, the Brillouin peaks no longer increase in frequency as the volume fraction increases. Furthermore, a second Brillouin peak appears at higher frequencies for the two larger volume fractions, albeit at much lower intensity. As q increases still further, these changes become more pronounced, as the two Brillouin modes are clearly resolved for the two larger volume fractions, and are of roughly equal intensities. This behavior is illustrated by the spectra for ϕ_c=0.16, 0.38 and 0.51 for the smaller spheres, with $q\approx$0.026 nm^{-1}, corresponding to $qd\approx 2.8\pi$, shown in Fig. 3. For the lowest volume fraction, ϕ_c=0.16, only one mode can be resolved, although its shape is perhaps slightly asymmetric, suggesting that the two modes may still exist, but their frequencies may not be sufficiently separated to clearly resolve the peaks. Both Brillouin peaks correspond to longitudinal modes as confirmed by the absence of any depolarized scattering.

To summarize the behavior of both Brillouin modes, we plot the dispersion relations for the smaller spheres in Fig. 4, for three different volume fractions, ϕ_c=0.16, 0.38, 0.51, corresponding to effective hard sphere volume fractions of ϕ=0.21, 0.49, and 0.64. For comparison, we also show the linear dispersion curves for the longitudinal sound modes that would exist in the pure phases. The dashed line corresponds to the solid PMMA, while the solid line corresponds to the pure index–matching fluid. The values of the velocities used to plot these dispersion curves are obtained from experimental measurements made at very high qd using the larger spheres, as discussed later.

There are several remarkable features in the dispersion curves shown in Fig. 4. At low q, only a single mode is observed for all ϕ, with linear dispersion as q goes to zero. The frequencies of this mode increase with increasing volume fraction of PMMA. However, as q increases further, the dispersion curves for all three volume fractions begin to flatten and the frequency for the higher volume fractions actually drops below that of the lower volume fractions. For ϕ_c above 0.16, the second, higher frequency mode appears at $q\approx$0.009 nm^{-1}, corresponding to $qd\approx\pi$. This mode persists as q increases, and the splitting between the two modes increases with increasing volume fraction. At the lowest volume fraction, the measured frequency of the mode is nearly unchanged from that of the index matching fluid.

At higher volume fractions, two distinct modes are resolved for q above 0.009 nm^{-1}, corresponding to $qd>\pi$. The velocity of the higher frequency mode lies between the velocities of the pure liquid and solid phases. In addition, its velocity increases with increasing volume fraction. This behavior is expected for a mode that is characteristic of a composite medium. By contrast, the behavior of the lower frequency mode is much more

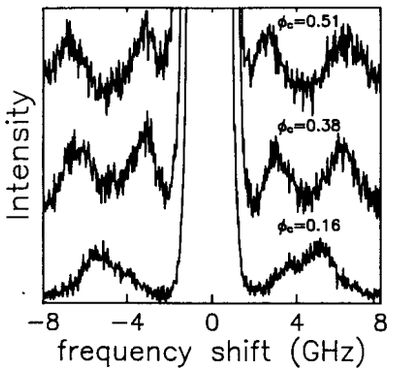


Figure. 3.
Brillouin spectra for three different volume fractions of 370 nm diameter spheres measured at q=0.026 nm^{-1}, corresponding to $qd=2.8\pi$. The two distinct modes are clearly observed for the two higher volume fractions.

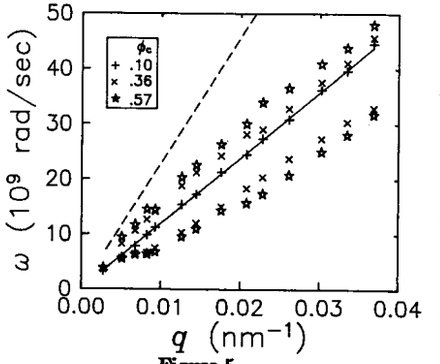


Figure 5.
The dispersion curves for the longitudinal acoustic modes for three different volume fractions of the 680 nm diameter spheres. The lowest volume fraction exhibits only a single mode, while the two higher volume fractions exhibit two modes above $q\approx$.005 nm^{-1}. The splitting between the modes increases with volume fraction. The solid line is the dispersion curve for the longitudinal mode in the pure index-matching fluid, while the the dashed line is the dispersion curve for pure PMMA.

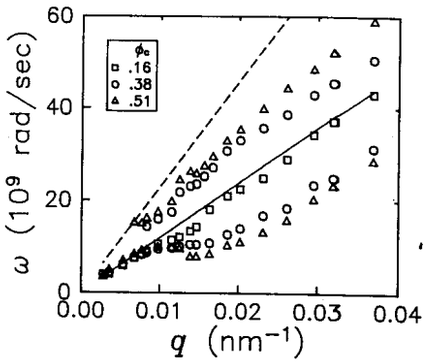


Figure 4.
The dispersion curves for the longitudinal acoustic modes for three different volume fractions of the 370 nm diameter spheres. The lowest volume fraction exhibits only a single mode, while the two higher volume fractions exhibit two modes above $q\approx$.009 nm^{-1}. The splitting between the modes increases with volume fraction. The solid line is the dispersion curve for the longitudinal mode in the pure index-matching fluid, while the the dashed line is the dispersion curve for pure PMMA.

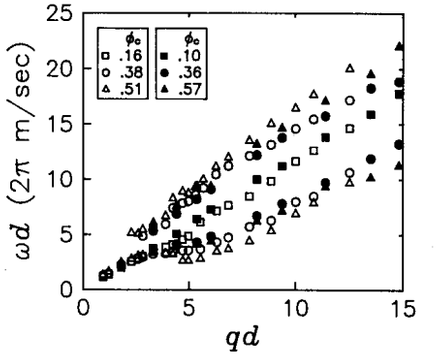


Figure 6.
Scaled dispersion curves for the two different sphere sizes. Each axis is scaled by the core diameter of the spheres, 340 and 650 nm. The solid symbols refer to the larger spheres and the open symbols refer to the smaller spheres. The scaled data exhibit similar but not identical behavior.

unusual and unexpected. Its velocity lies below that of the slowest velocity of any pure phase that makes up the medium. In addition, its velocity *decreases* with increasing volume fraction. Finally, the frequencies of both modes for all three volume fractions soften around the peak in the static structure factor, which occurs at $q\approx$0.015 nm^{-1}, corresponding to $qd\approx 2\pi$. The softening of the lower frequency mode is considerably more pronounced, and the degree of softening increases with volume fraction.

To investigate the behavior at even larger values of qd, and to compare the behavior for different sphere sizes, we also measured the dispersion curves with the larger spheres. These are shown in Fig. 5 for core volume fraction of ϕ_c=0.10, 0.36 and 0.57. The overall trend of the dispersion curves are the same as for the smaller spheres. At the very lowest value of q only a single mode is observed, while for all larger values of q, two distinct modes are again observed. In addition, the splitting between the two modes again increases with increasing ϕ_c.

To compare the behavior of the different sphere sizes, we scale the two sets of data together. This is accomplished by multiplying each axis by the sphere diameter, d. Thus, on the horizontal axis, we plot qd, which is a dimensionless quantity, while on the vertical axis, we plot ωd, which has units of velocity. The vertical axis could be made dimensionless as well by normalizing by velocity. This scaling ensures that the dispersion curves of the pure phases exhibit the proper scaling behavior. The two sets of scaled dispersion curves are shown in Fig. 6, where we only plot the region of qd for which overlapping data is available. The solid points refer to the data for the larger spheres, with core diameters, d_c=650 nm, while the open points refer to the data for the smaller spheres, with d_c=340 nm. As expected, the scaled data for the two sphere sizes do exhibit the same trends: the splitting of the modes occurs at the same point, $qd\approx\pi$, for both data sets, and both sets of data exhibit a softening around $qd\approx 2\pi$. However, the scaling of the data is not exact. The degree of softening of the modes at $qd\approx 2\pi$ is substantially less pronounced for the larger spheres than for the smaller spheres. Furthermore, the splitting between the normalized frequencies of the two modes is consistently less pronounced for the larger spheres than for the smaller spheres. Thus, the high frequency mode of the larger sized spheres always has a lower normalized frequency for a given value of qd and ϕ_c than that of the smaller sized spheres. Similarly, the low frequency mode of the larger spheres always has a larger normalized frequency for a given value of qd and ϕ_c than that of the smaller spheres. Consequently, a larger volume fraction of spheres is required for the larger sized spheres to clearly resolve the two modes.

In addition to the inexact scaling of the data of the different sized spheres, the dispersion curves of the larger spheres exhibit a clear trend as qd increases. To illustrate this more clearly, we plot the phase velocities, $v=\omega/q$, of the two modes for several volume fractions of the larger sized spheres in Fig. 7. The velocity for ϕ_c=0.10 is again almost indistinguishable from that of the index matching fluid. By contrast, for higher volume fractions, the velocity of the higher frequency mode is initially much greater than that of the fluid, but as qd increases, the velocity decreases, and in fact appears to asymptotically approach that of the pure fluid. In addition, the velocity of the lower frequency mode displays a softening at $qd\sim 2\pi$, but as qd increases, it seems to approach a constant value that is well below that of the index-matching fluid.

Finally, at the highest values, $qd\approx 25$, an additional weak mode appears in the spectra, at higher frequencies. We attribute this new mode to the propagation of sound in the bulk solid. The velocity of this mode is close to that measured for solid PMMA, and thus is consistent with sound propagation within the bulk of the spheres. This is expected at these high values of qd, where several wavelengths of sound can fit into each sphere. It is not surprising that the velocity of sound is somewhat different than bulk PMMA, as the fabrication process of the colloids presumably produces a polymer with a somewhat different elastic modulus. However, since qd is so high, this new mode probably does not reflect a wave that propagates between adjacent spheres, but rather reflects propagation confined within a single sphere.

Further insight into the behavior of the acoustic propagation is obtained from the damping of the Brillouin modes, determined from the measured full widths at half maximum intensities, $\delta\omega$. We characterize the damping by means of the quality factor, $Q=\omega/\delta\omega$, which reflects the number of wavelengths the sound wave propagates. We plot the quality factors measured for the smaller spheres as a function of qd in Fig. 8. As qd approaches zero, the lower frequency mode is very well defined, as indicated by a large value of Q. However, by the time qd reaches about π, the value of Q for the lower frequency mode has decreased and remains constant at about 2, independent of qd. By contrast, the Q of the higher frequency mode exhibits a pronounced resonance around $qd\sim 2\pi$, reflecting a decrease in the damping of the mode. The behavior of Q for the larger spheres consistent with that shown for the smaller spheres in Fig. 8, but the resonance at $qd\sim 2\pi$ for the higher frequency mode is not as pronounced, since the resolution in qd is not as high with the larger spheres.

Figure 7.
The phase velocities of both modes for three different volume fractions of the 680 nm diameter spheres, plotted as a function of qd. Only one mode is present for the lowest volume fraction, and its velocity is nearly identical to that in the pure index-matching fluid. The two higher volume fractions exhibit two modes. The velocity of the faster mode is highest around $qd\approx\pi$, and then decreases as qd increases, ultimately asymptotically approaching that of the index-matching fluid. The slower mode exhibits a decreasing velocity as qd approaches 2π, but then the velocity increases at higher qd, ultimately becoming roughly constant, at a value equivalent to that expected for a Stonely wave at a flat interface.

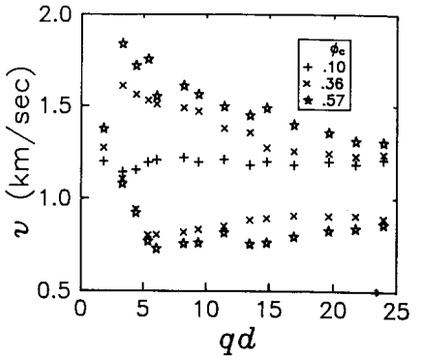
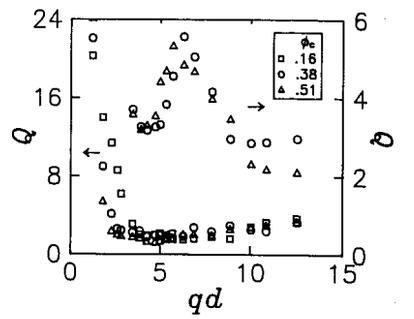


Figure 8.
The quality factors, $Q=\omega/\delta\omega$, for the two modes for three different volume fractions of the 370 nm diameter spheres plotted as a function of qd. The higher frequency mode exhibits a pronounced peak around $qd\approx 2\pi$.



DISCUSSION

The most surprising feature of the dispersion curves for the suspension of hard sphere colloids is the existence of two distinct modes. For these systems, the continuous phase is a fluid, which has no long range rigidity, and thus can not support shear. Thus, only a single longitudinal mode is expected. In fact, at very long sound wavelengths, this can be rigorously shown to be the case.[4] This same behavior is typically expected to persist to shorter wavelengths as well.[1] Therefore, the observation of two distinct modes when the wavelength of sound becomes comparable to the diameter of the spheres is unexpected.

The closest analogy to this behavior is that first proposed theoretically by Biot.[6] He considered the propagation of sound in a porous medium at long wavelengths and high frequencies. The characteristic frequency required is determined from the viscous penetration length, defined as $\ell=\sqrt{\rho/\eta\omega}$, where ρ is the density of the solid and η is the viscosity of the fluid. This is the length scale of viscous coupling of transverse waves from the solid into the fluid. When the frequency is sufficiently high that ℓ is less than the pore size, the Biot theory applies. Then, the solid and the fluid become decoupled, with one sound mode propagating through the solid phase, and a second, new mode propagating through the fluid phase. This new, slow mode is a wave that propagates predominantly in the fluid, but its velocity is slower than that in the pure fluid phase because of the tortuosity of its path. The veracity of Biot's prediction has been confirmed, both for sound propagation in some porous media structures[7] and for sound propagation through super fluid helium in a porous medium.[8] However, for the Biot theory to apply, the solid phase of the porous medium must be a contiguous, rigid structure and the solid and fluid must form interconnecting phases. This is not the case for a suspension of hard sphere colloids. Because of the grafted polymer stabilizing layer, the solid spheres are not interconnected, even at the highest volume fractions studied. Furthermore, while the fluid phase is clearly completely interconnected, its tortuosity is very nearly unity,[9] so the decrease in the sound velocity of the lower frequency mode can not be ascribed to a Biot slow wave. Thus, the Biot approach can not describe the behavior that we observe.

The data suggest an alternate physical picture of the origin of the two modes. The higher frequency mode has a velocity that lies between that of the solid PMMA and the index-matching fluid. Furthermore, the frequency of this mode increases with increasing volume fraction. Thus the solid PMMA spheres must play an important role in the sound propagation for this mode and the acoustic wave must propagate through both the fluid and the solid phases. However, this mode is only observed when $qd > \pi$, suggesting that the sound propagates through the solid spheres only when it can excite internal resonances of the spheres. This will occur when a half wavelength of the sound can fit inside the sphere, or when $qd \sim \pi$. Since the velocity of sound in the solid is nearly twice that of the fluid, when the acoustic excitation involves a larger proportion of solid spheres due to an increased ϕ, the velocity will increase.

As qd increases still further, the solid and liquid regions can behave increasingly independently, as more sound wavelengths fit into each region. The sound velocity of the higher frequency mode decreases, approaching the velocity in the pure liquid phase. This suggests that the velocity of this mode is increasingly dominated by that of the fluid, implying that the excitation is trapped to a grater extent in the fluid by the large acoustic impedance mismatch with the solid. Ultimately, at very large qd, a sufficient number of sound wavelengths can fit into the individual solid spheres or fluid interstices, and two distinct modes can be expected, corresponding to the velocities in the pure solid and pure fluid phases. This is exactly what is observed with the larger spheres at the largest scattering angles, corresponding to $qd \sim 25$. Presumably the dominant contribution to the Brillouin scattering is from the portion of the excitation in the liquid, where the compressibility is larger, leading to a larger scattering amplitude.

While the high frequency mode reflects sound propagation through both the liquid and the solid as might be expected for a composite medium, the lower frequency mode can not reflect this type of behavior. Its frequency corresponds to a sound velocity that is even lower than that of the index-matching fluid, the lowest sound velocity in a pure phase of the composite system. Furthermore, the frequency decreases as the volume fraction increases. The only slower propagating sound mode in a system comprised of a solid and a fluid is a Stonely wave, which is a propagating mode confined to an interface between a solid and a fluid.[10] It is analogous to a Raleigh wave which is a propagating mode confined to the interface of a solid and a vacuum. The existence of a Stonely wave requires a shear modulus in the solid. It consists of both longitudinal and transverse components in the solid with a purely longitudinal component in the fluid. Its magnitude decays exponentially away from the interface, both in the fluid and in the solid. Using the known longitudinal and transverse velocities in bulk PMMA and the measured velocity in the fluid, we calculate the velocity of the Stonely wave on a flat interface to be about 860 m/sec. As shown in Fig. 7, this corresponds remarkably well to the velocity measured at high qd for the larger spheres, where the interface is nearly flat. At smaller qd, where the wavelength is comparable to the size of the spheres, the measured value of Q implies that the excitation propagates over distances larger than a single sphere. Thus, at low qd, this mode must represent some form of coupled Stonely wave where the longitudinal component in the fluid couples the excitation between adjacent spheres. This accounts for the fact that the splitting between the two modes is less for a given volume fraction of the larger spheres than for the same volume fraction of the smaller spheres. The average distance between the spheres scales with the sphere size, and thus the coupling between adjacent spheres through the exponentially decaying longitudinal fluid portion becomes more difficult with increasing sphere size. This accounts for the inexact scaling of the data from different sphere sizes. Finally, in the region of low qd, the softening of the mode around $qd \sim 2\pi$, near the peak in the structure factor, implies that the scattering of the wave from the different spheres becomes more significant. Furthermore, as shown in Fig. 8, the low values of the Q factor for this mode are also consistent with the large degree of scattering.

There have been some previous experimental studies of sound propagation in similar systems, usually using glass rather than polymer spheres.[1] Typically these studies used ultrasonic techniques to measure the actual propagation of sound through the system, and usually they were restricted to sound wavelengths that were small compared to the size of the spheres. Thus, two modes were never seen. In addition, there have been some theoretical treatments of sound propagation through hard sphere systems that used multiple scattering formalism.[11] However, these studies were restricted to low qd, and thus did not predict the existence of two modes. More recently, numerical calculations on a two dimensional system of disks embedded in a fluid have included the shear modulus for the solids.[12] They have predicted the existence of two modes, in remarkable agreement with the experimental observations reported here. Furthermore, the predicted behavior of the two modes is similar to that observed: the lower frequency mode is predominantly an interfacial mode comprised of a transverse component in the solid, while the higher frequency mode is an longitudinal mode that extends through the bulk of both the fluid and the solid, and is increasingly confined to the fluid at higher qd.

CONCLUSIONS

In this paper, we have presented the results of a study of sound propagation through a suspension of hard sphere colloids. We use PMMA spheres immersed in an index-matching fluid, eliminating any multiple scattering of light. This enables us to use Brillouin scattering to measure the thermally excited sound waves in the system. By varying the scattering angle, as well as the sphere size, we are able to probe the frequency of the propagating acoustic modes over values of qd extending from about 1 to 25. Surprising results are obtained. Even though the continuous phase is a fluid, and thus can support only single propagating longitudinal mode, two distinct acoustic modes are found for $qd > \pi$.

We interpret the higher frequency mode as an excitation that propagates within both the liquid and the solid phases, as expected for a composite medium. As the volume fraction of solids increases, the excitation is increasingly within the solid phase, accounting for the increase in the velocity with increasing ϕ. We interpret the lower frequency mode as an interface or Stonely wave, which is the only mode that can propagate at a velocity slower than the velocity in the pure fluid. This excitation must propagate between adjacent spheres and thus must be coupled through the longitudinal portion in the fluid.

These hard sphere colloid systems have been of great interest recently because of their fascinating phase behavior. The results of this paper suggest that their high frequency dynamic properties, as evidenced by the propagation of acoustic waves through the systems, also exhibits fascinating behavior.

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