Novel Acoustic Excitations in Suspensions of Hard-Sphere Colloids

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We use Brillouin scattering to measure the longitudinal-phonon dispersion curves for a suspension of hard-sphere colloids. Two distinct propagating acoustic excitations are observed when the wavelength of the sound is comparable to, or smaller than, the size of the spheres. One excitation has a velocity intermediate between that of the fluid and the solid phases and is interpreted as an acoustic wave propagating through the composite medium of fluid and solid spheres. The second has a velocity slower than both that of the solid and that of the fluid phase and is interpreted as a coupled interfacial, or Stoneley, wave.

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The propagation of acoustic waves through random composite media comprised of solid and fluid components is a problem of immense practical importance because of its utility for seismic investigations and other nonintrusive probes; it is also of great fundamental interest because of the rich variety of fascinating phenomena that have been observed. One of the simplest and most fundamental structures consists of uniform solid spheres immersed in a fluid.[1] The characteristics of a suspension of spheres are highly controllable, as the particle size, solid volume fraction, and acoustic wavelength can all be independently varied. The acoustic scattering properties of the constituent particles, isolated spheres in a fluid, are well known,[2] having been studied at least from the time of Lord Rayleigh.[3] The acoustic propagation in suspensions of spheres has been studied extensively experimentally for wavelengths λ large compared to the sphere diameter d.[1,4] It has also been treated successfully theoretically using an approach which considers the multiple scattering of waves in the fluid by the solid spheres.[1] The behavior when λ becomes comparable to d has been much less extensively investigated experimentally. This regime is of considerable interest, however, both because of the possibility of resonant scattering effects and because it is when $\lambda \sim d$ that the localization of classical acoustic waves is expected.[5,6] Since only the fluid phase is continuous, this medium lacks long-range rigidity and cannot support shear. Thus, it can be shown[7] rigorously that only a single longitudinal sound mode can propagate at long wavelengths, $\lambda > d$. Similarly, only a single longitudinal mode is expected at shorter wavelengths as well. In this Letter, we present the first comprehensive experimental results on the acoustic propagation in a suspension of hard spheres. We show that, contrary to expectations, when λ becomes comparable to or smaller than d, there are not one, but two distinct propagating longitudinal sound modes.

We use Brillouin scattering to measure the frequency of the thermally excited propagating longitudinal sound modes in suspensions of hard-sphere colloids of varying volume fraction of solids, ϕ. Since the colloid diameters are comparable to the wavelength of light, the use of Brillouin scattering allows us to easily vary the size of the acoustic wavelength relative to the sphere diameter, simply by varying the scattering wave vector q. We are thus able to measure the dispersion curves over a wide range of qd. When λ is substantially larger than d, we see only a single longitudinal mode, whose frequency increases with ϕ. However, when λ becomes comparable to d, two distinct sound modes are observed. One mode has a velocity intermediate between that in the pure solid phase and the pure fluid phase. Furthermore, the sound velocity of this mode increases with ϕ. We suggest that this mode propagates through both the fluid and the solid. This mode exhibits pronounced gaps in its frequency spectrum corresponding to the excitation of internal vibrational resonances of the spheres, where the strong scattering cross section inhibits the propagation of the excitation. The other mode has a velocity that is significantly lower than the sound velocity of any constituent pure phase in the medium. Furthermore, this velocity *decreases* as ϕ increases. We suggest that this mode reflects a propagating interfacial, or Stoneley, wave that is coupled between adjacent spheres through the component of the excitation in the fluid. The existence of two distinct longitudinal modes has, to our knowledge, never been observed.

We study a hard-sphere colloid system that has been of great interest in its own right,[8] as it exhibits a rich phase behavior that possesses strong analogies to that of a simple, hard-sphere atomic system. At low ϕ, the colloidal particles behave as a fluid, while for ϕ above 0.49, the colloidal particles form either a colloidal glass or a colloidal crystal. Our samples are monodisperse polymethylmethacrylate (PMMA) spheres, with diameters of 370 or 680 nm. They are sterically stabilized by a thin layer of grafted polymer, with a thickness of about 15 nm, so their core diameters are $d_c = 340$ and 650 nm. The colloidal particles are immersed in an index-matching mixture of dodecane and carbon disulphide, eliminating multiple light scattering. Because of the grafted-polymer layer, the solid PMMA cores of the colloids are disconnected, even at the highest volume fractions. The acoustic properties[9] depend on volume frac-

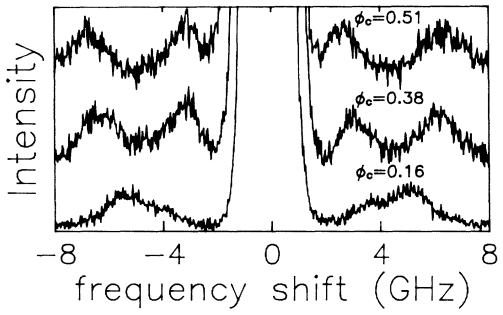

FIG. 1. Brillouin spectra obtained at $\theta=90°$, corresponding to $qd_c=2.8\pi$, using the colloids with $d_c=340$ nm.

tion of the solid PMMA, or core volume fractions ϕ_c. The Brillouin scattering is performed using single-mode Ar^+ or Kr^+ lasers with wavelengths of 5145 or 6471 Å, respectively. The scattered light is imaged onto a 150-μm-diam pinhole and then collimated into a five-pass Fabry-Pérot interferometer. Unlike ultrasonic probes of acoustic propagation, in these experiments, the scattering wave vector is well defined, determined by the experimental geometry, and the frequency is measured, at fixed q, from the Brillouin peaks.

The lowest scattering angle used was $\theta\approx 9°$, which corresponds to $qd_c\approx 1$ for the smaller spheres, $d_c=340$ nm. The behavior here is still within the hydrodynamic regime, and we observe a single Brillouin peak in the spectra for all volume fractions. The sound velocity, determined from the frequency of this peak, $v=\omega/q$ increases with increasing ϕ_c, and is well described using an effective-medium theory.[9,10] As qd_c increases above π, a dramatic change is observed in the Brillouin spectra. This is illustrated in Fig. 1, where we show spectra for spheres with $d_c=340$ nm, for three different volume fractions, $\phi_c=0.16$, 0.38, and 0.51, obtained at $qd_c\approx 2.8\pi$. At the higher ϕ_c, there are not one, but two Brillouin peaks, and their frequency splitting increases with ϕ_c. The higher-frequency mode is initially much less intense than the lower-frequency mode, but increases in intensity as qd_c increases, and ultimately becomes more intense at large qd_c. At low ϕ_c, only one peak is observed, although its shape is clearly asymmetric, suggesting that the two modes still exist, but with insufficient splitting to clearly resolve them. All the Brillouin peaks correspond to longitudinal sound modes as confirmed by the absence of depolarized scattering.

To determine the qd_c dependence of the two modes, we plot their dispersion relations in Fig. 2. For comparison, we also show the linear dispersion relations for the longitudinal sound modes in solid PMMA (dashed line) and in the index-matching fluid (solid line). There are several remarkable features in these dispersion curves. At low qd_c, only a single mode is observed for all ϕ_c, with a linear dispersion as qd_c goes to zero. For low ϕ_c, this single mode persists at all qd_c, and its frequency is

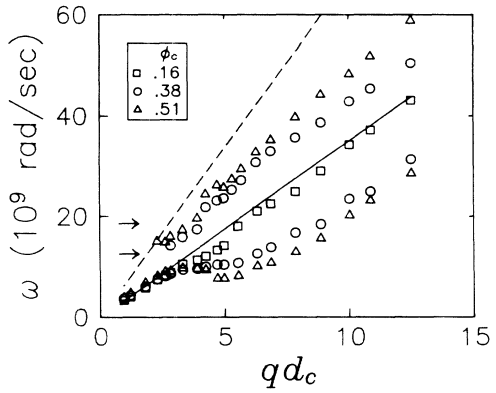

FIG. 2. The phonon dispersion curves for suspensions of hard-sphere colloids, with $d_c=340$ nm. The arrows indicate the frequencies of the peaks in the scattering cross section for isolated spheres of the same diameter.

nearly unchanged from that of the fluid. For $\phi_c\geq 0.2$, the single mode splits into two at $qd_c\approx\pi$, and both modes persist as qd_c increases. The higher-frequency mode lies between the frequencies of the pure solid and the pure liquid phase. Furthermore, its frequency increases with ϕ_c. By contrast, the lower-frequency mode lies well below that of the pure liquid phase. Furthermore, its frequency *decreases* with increasing ϕ_c. Finally, around $qd_c\sim 2\pi$, the frequencies of both modes decrease, with the softening of the lower-frequency mode considerably more pronounced.

To investigate the behavior at even larger qd_c, and to determine the scaling with sphere size, we measure the dispersion curves for the larger spheres, $d_c=650$ nm. The dispersion curves for the two sphere sizes are nearly identical if the frequencies and the wave vectors are both scaled by d_c. However, at higher qd_c, the data for the larger spheres exhibit a distinguishing trend. To illustrate this, we plot the phase velocities $v=\omega/q$ of the two modes for several volume fractions of the larger spheres in Fig. 3. The velocity for $\phi_c=0.1$ is again almost indis-

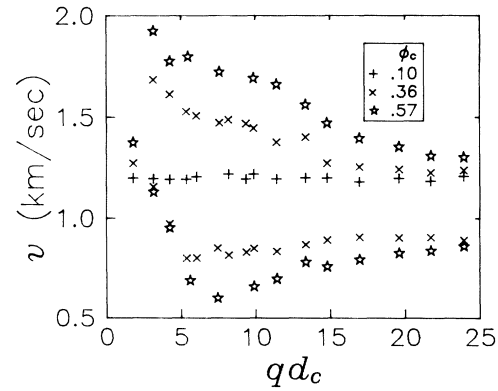

FIG. 3. The phase velocities for suspensions of hard-sphere colloids with $d_c=650$ nm.

tinguishable from that of the fluid at all qd_c. For higher ϕ_c, the velocity of the higher-frequency mode is again initially much greater than that of the fluid. However, as qd_c increases, the velocity *decreases,* and appears to asymptotically approach that of the fluid. By contrast, the velocity of the lower-frequency mode displays a softening at $qd_c \sim 2\pi$, but as qd_c increases, it approaches a constant velocity well below that of the fluid.

The most pronounced and remarkable feature of the data is the presence of two distinct longitudinal modes. The closest analogy to this behavior is that first predicted by Biot,[11] and later observed,[12] for high-frequency, long-wavelength sound propagation in a porous medium. When the frequency is sufficiently high that viscous penetration length l is less than the pore size, the fluid and the solid are no longer viscously coupled, and two longitudinal sound modes exist. In the first mode, the motions of the fluid and the rigid solid frame are in phase, and the velocity is very nearly that of the solid. In the second mode, the motions of the fluid and the solid are out of phase, and the excitation is predominantly confined to the fluid. The velocity is decreased from that of the pure fluid because of the tortuous path the sound wave must follow. In our experiments, $l \sim 15$ nm, but the grafted polymer ensures that the spheres are separated by at least 30 nm, even at the highest ϕ, so the spheres are not viscously coupled through the fluid. However, a suspension of hard-sphere colloids does not possess a consolidated, rigid frame, as required by the Biot theory. In addition, the observed decrease in the velocity of the low-frequency mode cannot be due to an increased tortuosity as the calculated value of a hard-sphere system is nearly unity.[13] Thus our results cannot be described by the Biot theory.

There are several physical features that any theoretical model must capture. The high-frequency mode must reflect an excitation propagating in both the fluid and the solid, since its velocity is intermediate between those of the two pure phases and increases with ϕ. This same behavior characterizes the single mode at low q, suggesting that it is the high-frequency excitation which is a continuation of the single mode that exists when $qd_c < \pi$. Thus, a pronounced frequency gap exists where no excitation can propagate. The frequency of the gap correlates exactly with the lowest-frequency peak in the scattering cross section predicted for a single, isolated PMMA sphere in the index-matching fluid, corresponding to the excitation of an internal vibrational mode. In fact, a second, less pronounced, gap in the dispersion curve exists at a higher frequency corresponding to the next peak in the single-sphere scattering cross section, although this is somewhat obscured by the overlap of the data from different ϕ_c. The calculated[14] frequencies of the first two single-sphere resonances are shown by the arrows in Fig. 2, and the resultant high scattering cross section of the spheres inhibits the propagation of the excitation, opening the gaps in the dispersion curve. Further evidence of the importance of internal resonances of the spheres is provided by the behavior of the damping of the mode determined from the measured full width at half maximum of the Brillouin peaks, $\delta\omega$. In Fig. 4, we plot the quality factor $Q = \omega/\delta\omega$, which reflects the number of wavelengths the mode propagates. The higher-frequency mode exhibits a resonance in Q near $qd_c \sim 2\pi$, reflecting the effects of an internal resonance within the spheres. Finally, as qd_c increases still further, the sound velocity of the higher-frequency mode is increasingly dominated by that of the fluid. Because of the large acoustic-impedance mismatch, total internal reflection limits the propagation of the excitation from the low-velocity fluid into the high-velocity solid, trapping it to a large extent in the fluid, and accounting for the asymptotic value of v at high qd_c. Ultimately, at very large qd_c, we expect to see two distinct modes, corresponding to the velocities in the pure solid and fluid phases. This is indeed observed using the larger spheres and the largest scattering angles, $qd_c \sim 25$, where a third mode appears, with a velocity close to that of solid PMMA.

The behavior of the low-frequency mode is perhaps even more surprising. Its velocity is even lower than that of the fluid, and *decreases* with ϕ_c. The small velocity suggests that this excitation may entail a Stoneley wave, a propagating mode confined to an interface between a solid and a fluid.[15] A Stoneley wave is distinguished by its slow velocity which is substantially lower than that of the fluid. It requires a shear modulus in the solid, and consists of both longitudinal and transverse components in the solid and a longitudinal component in the fluid. Its amplitude decays exponentially away from the interface. Using the known longitudinal and transverse velocities in bulk PMMA and the measured velocity in the fluid, we calculate[14] the velocity of the Stoneley wave on

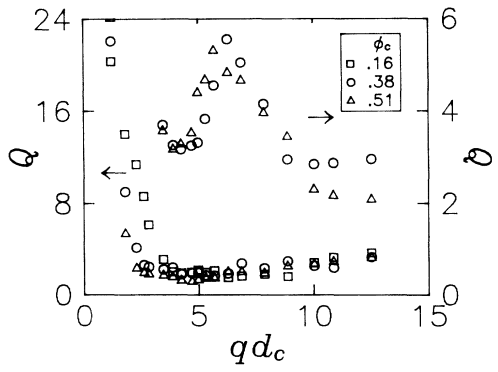

FIG. 4. The quality factors $Q = \omega/\delta\omega$ for the two modes as a function of qd_c for the colloids with $d_c = 340$ nm. To better illustrate the peak in Q near $qd_c \approx 2\pi$, the right-hand scale refers to the data for the higher-frequency mode for those cases when two distinct modes are observed. The left-hand scale refers to the remaining data.

a flat interface to be about 860 m/sec. As shown in Fig. 3, this corresponds remarkably well to the velocity measured at high qd_c for the larger spheres, where the interface is nearly flat on the length scale of λ. At smaller qd_c, where λ is comparable to d_c, the low-frequency excitation must extend beyond the interface into the sphere and the fluid. Furthermore, the measured values of $Q \approx 3$ imply that the excitation propagates coherently to adjacent spheres. This coupling to adjacent spheres must entail the exponentially decaying longitudinal component of the excitation in the fluid, and will increase in strength as the separation of the spheres decreases. This explains the unusual ϕ_c dependence of the velocity: As ϕ_c increases, the excitation propagates along more interface where the velocity is lower, and through less fluid where the velocity is higher, thus resulting in a net decrease in v. Furthermore, for a given ϕ_c, the coupling should become weaker with increasing d_c since the average sphere separation scales with diameter. This is indeed observed as the onset of the mode splitting occurs at a consistently higher ϕ_c for the larger spheres than for the smaller ones. Finally, the coupling to adjacent spheres also makes the low-frequency mode highly sensitive to the *relative* positions of the spheres, and thus to the structure factor. This is reflected in the dispersion relations by the softening near $qd_c \sim 2\pi$.

Both the internal vibrational resonances in the spheres, which result in the gaps in the dispersion curves, and the coupled Stoneley wave excitation depend critically on the presence of a shear modulus in the spheres. This suggests that the scalar wave equation may not suffice, but that the full elastic wave equation must be used to successfully account for the observations. Indeed, stimulated by these results, recent numerical and analytical calculations[14] using the elastic wave equation to treat two-dimensional disks immersed in a fluid have confirmed the existence of two distinct longitudinal modes with calculated dispersion curves remarkably similar to those observed in our experiments. Finally, the presence of two distinct longitudinal modes, and the necessity to use the elastic wave equation, will also have profound consequences for any possible localization of acoustic waves, which have not been considered to date. We conclude by emphasizing that, despite over 100 years of study, the acoustic properties of suspensions of hard-sphere colloids still exhibit unexpected and rich behavior which has yet to be fully explored.

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