

Acoustic Excitations in Suspensions of Soft Colloids

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Vibrational modes in suspensions of soft colloids in a fluid can be detected experimentally by Brillouin light scattering. Besides the usual acoustic mode, being essentially the longitudinal phonon of the liquid matrix, an “opticlke” mode is observed in giant starlike micelles at low volume fractions. We propose that this opticlke mode is due mainly to the internal vibration of each hairy particle.

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The propagation of acoustic waves through inhomogeneous media has long been the subject of interest, due to fascinating rich behavior, and practical relevance, as a result of their use for nondestructive testing [1–4]. For suspensions of hard-sphere colloids in a fluid that cannot support shear, one [5] or two [6] propagating longitudinal phonons were observed. Besides the value qd (q is the sound wave vector and d is the solid particle diameter), acoustic propagation appears to relate to the viscous coupling of a neighboring sphere [5]. The higher frequency acoustic mode, with phase velocity intermediate between those of the pure solid and liquid components, was attributed to the composite medium while the lower frequency mode was interpreted as a surface acoustic (Stonley wave) excitation; the spheres were sterically stabilized by a thin (~ 15 nm) layer of grafted polymer. The two distinct modes appear when the wavelength of the phonon is about twice the diameter of the spheres, i.e., $qd \approx \pi$ and for high volume fractions ($\phi > 0.3$) of the spheres. In contrast, smaller spheres [5] at similar qR exhibit one propagation sound mode displaying a counterintuitive softening with increasing ϕ , i.e., with the amount of the high velocity material. These limited results obtained from Brillouin scattering have shown unexpected and still unexplored sound propagation behavior in colloidal suspensions. In this Letter, we present the first experimental results on the longitudinal sound propagation in a suspension of soft hairy spheres contrasting to the acoustic properties of the previous systems [7].

Spherical micelles formed by diblock polymers in a selective solvent for one of the blocks behave as soft colloids with the insoluble chains forming the core of mesoscopic radius R_i and the solvated chains forming the stabilizing polymer layer (corona). These systems exhibit liquidlike order at relatively low number densities [8] much like hard-sphere colloids. However, in contrast to the latter system [9], the long-time diffusion coefficient describing their structural relaxation exhibits no slowing down for distances of the order of the “cage” dimensions, probably due to polymer-layer mediated effects [10,11]. We employed

high resolution Brillouin spectroscopy to measure the dispersion of the thermally acoustic longitudinal modes. This study revealed the presence of one lower frequency phonon with velocity very similar to the pure fluid and a high frequency “opticlke” phonon with a flat ω vs q dependence. With an increasing amount of the hairy particles, the attenuation of the lower frequency phonon increases.

An asymmetric monodisperse styrene-isoprene (SI) diblock copolymer with average molecular weight 1.9×10^6 g/mol and styrene weight fraction 0.26 was obtained by anionic polymerization. Solubilization in *n*-decane led to giant micelles consisting of 1470 SI chains with insoluble glassy polystyrene [core radius $R_i = 58$ nm and polyisoprene shell with an overall radius $R_e = 353$ nm obtained from the form factor at dilute conditions (2.5×10^{-3} wt%)] [10]. Development of liquidlike ordering starts at concentrations higher than about 0.8 wt%. The phonon propagation in suspensions of weakly interacting soft micellar particles was monitored by Brillouin light scattering spectroscopy in the GHz frequency range. Brillouin spectra arising from the propagating thermal density fluctuations [12] in the system were recorded by a tandem Fabry-Perot interferometer (TFPI) [13]. A split weak laser beam ($\lambda = 514.5$ nm) was utilized to stabilize the TFPI during the recording period of the elastic central Rayleigh peak by means of a synchronized shutter.

The frequency of the longitudinal phonon is measured from the Brillouin peaks at a fixed wave vector q , determined by the scattering angle. In homogeneous media, one Brillouin doublet $\pm\omega$ Doppler shifted about the central Rayleigh line is observed and the phase velocity c of the longitudinal phonon is ω/q . For example, this is the case for a solution of small starlike micelles ($R_e = 10$ nm) [10]. Figure 1 shows typical Brillouin spectra of SI suspensions for 0.29 wt% at three scattering wave vectors corresponding to $qR_i = 0.4, 0.75,$ and 1.6 . Two Brillouin doublets are already clearly observed at low concentrations prior to the onset of significant interparticle interactions. The lower frequency phonon compares well to the longitudinal phonon of the solvent, and its frequency

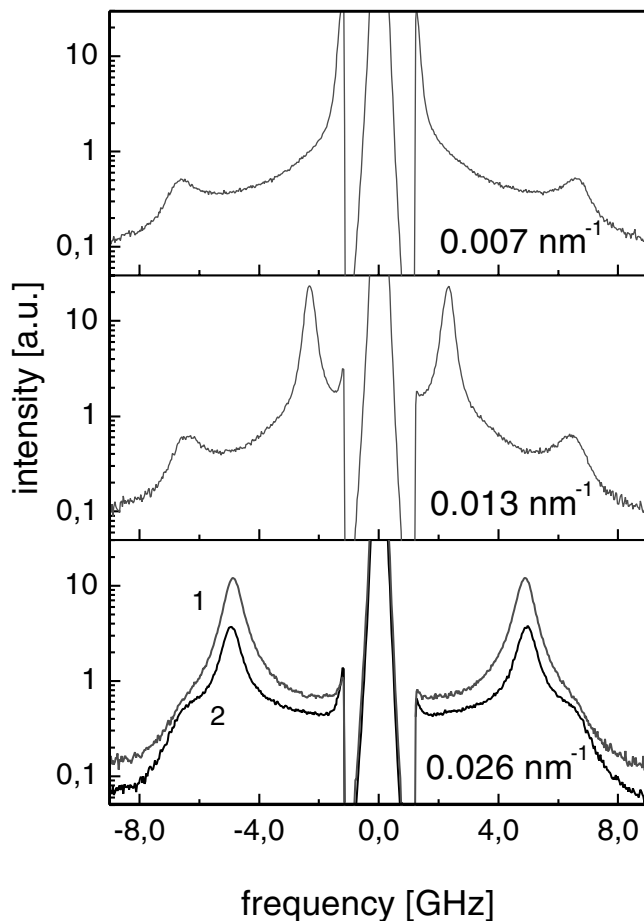


FIG. 1. Rayleigh-Brillouin spectra obtained at three different scattering angles corresponding to $q = 0.007$, 0.013 , and 0.026 nm^{-1} for 0.29 wt% soft particles in *n*-decane at 20°C . The comparison of the spectra for 0.29 wt% (curve 1) and 0.73 wt% (curve 2) is made at $q = 0.026 \text{ nm}^{-1}$ in the lowest part of the figure. For the sake of clarity, the spectrum (curve 2) is shifted by a factor of 2. The frequency region $\sim \pm 1 \text{ GHz}$ about the central peak is provided to the reference beam used for the stabilization of the tandem Fabry-Perot interferometer. The peaks of the lower frequency Brillouin doublet at $q = 0.007 \text{ nm}^{-1}$ are apparently shifted into this central frequency region for the used free spectral range (15 GHz).

is proportional to q . In the frequency range $\pm 1.1 \text{ GHz}$ about the central line, the scattering from the suspension is shut out and the TFPI is stabilized by the reference beam. Hence, the lower frequency phonon of Fig. 1 can hardly be seen at $q = 0.007 \text{ nm}^{-1}$. In contrast, the higher frequency phonon ($\sim 6.3 \text{ GHz}$) shows very weak dispersion and relates to the presence of the giant micelles. The neat solvent expectedly displays only the lower frequency phonon, whereas the higher frequency peak becomes more pronounced in denser particle solution. This is illustrated in Fig. 1 by displaying two spectra for 0.29 wt% (curve 1) and 0.73 wt% (curve 2) at the same q .

Figure 2 shows the sound dispersion relation $\omega(q)$ for the two phonons of Fig. 1 for 0.29 wt% suspension. The form factor of the latter depicted in the inset of Fig. 2 led

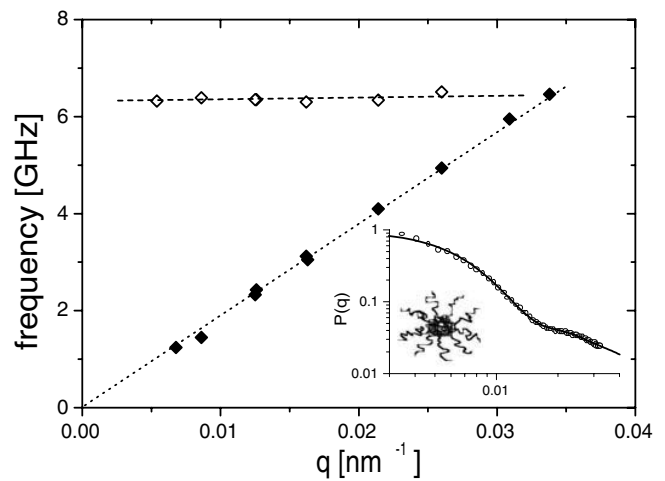


FIG. 2. The phonon dispersion for the soft starlike particles with an effective volume fraction $\phi \approx 0.1$. The open and solid points are for the opticlike and “acoustic” modes. Inset: The particle form factor along with its theoretical representation assuming starlike topology with inhomogeneous density and hence refractive index profile [9].

to the core size and layer thickness of the present starlike micelles [10]. A linear relation $\omega_s = cq$ was found for the lower frequency phonon which at these particle concentrations compares well to the acoustic phonon propagation in the solvent. The width of this Brillouin peak represents the acoustic phonon lifetime showing the expected hydrodynamic q^2 dependence.

It is the insensitivity of the second phonon to the q variation and its appearance at rather low soft particle concentration that is most surprising. This behavior should be contrasted to the hard-sphere colloids where the high frequency phonon was observed at volume fraction ϕ higher than 0.3 and further exhibits a clear q dependence; an even larger concentration was required for the larger rather than for the smaller spheres to observe the second acoustic excitation [6].

To quantitatively explain our results, we model each particle as a coated sphere with the solid core and fluid coating embedded in the solvent. The density (ρ), the longitudinal (c_l), and the shear (c_s) velocities are $\rho_i = 1050 \text{ kg/m}^3$, $c_{li} = 2800 \text{ m/s}$, $c_{si} = 1084 \text{ m/s}$ for the core; $\rho_c = 820 \text{ kg/m}^3$, $c_{lc} = 1170 \text{ m/s}$, $c_{sc} = 0$ for the coating; $\rho_0 = 730 \text{ kg/m}^3$, $c_{l0} = 1150 \text{ m/s}$, $c_{s0} = 0$ for the solvent. The core radius and the external coating radius are $R_i = 58 \text{ nm}$ and $R_e = 353 \text{ nm}$, respectively. $V_0 = V/N$ is the average volume per particle (V and N are the volume and the particle number of the system, respectively).

The flatness in q space of the high frequency mode strongly suggests that it is a local mode in real space associated with each particle. If this conjecture is correct, this mode should appear as a resonance (that is, a sharp peak) in the cross section of the scattering of a plane sound wave by a single particle. We did calculate this scattering cross

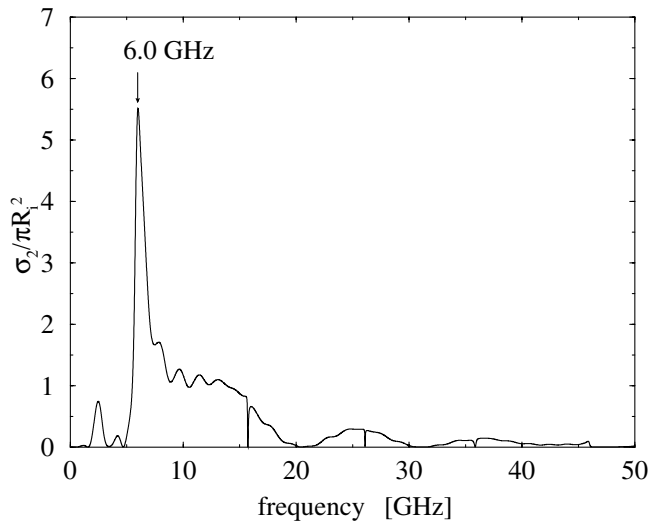


FIG. 3. The normalized scattering cross section versus frequency for a plane sound wave scattered by a coated sphere, and for the $\ell = 2$ spherical wave.

section, following the formalism presented in Ref. [14], and indeed we found a sharp d resonance (i.e., a peak in the $\ell = 2$ spherical harmonic component) at the frequency of 6 GHz (see Fig. 3) that is close to the observed frequency of 6.3 GHz. The angular dependence of this mode resembles that of the d orbitals in atoms.

Next, we calculated the distribution of energy density at the resonance frequency, to check whether this mode is localized in real space as suggested by the flatness in q space (see Fig. 2). We found that the energy density is well localized inside the core, which means that the high frequency d mode is confined mostly within the core (Fig. 4). Such a localized mode should interfere very weakly with similar modes associated with the other particles, explaining thus the observed flatness in q space.

To check the possibility of interference effects, we repeated our *sound* scattering calculation by a cluster of particles (up to 41 of them) including multiple scattering. We found no appreciable change in the position and width of the resonance. Furthermore, we estimated the intensity of light scattering by taking into account that these vibrations produce density variations proportional to the divergence of the displacement vector, \mathbf{u} . The light is scattered by the change, $\delta\epsilon$, in the permittivity [12], resulting from the change in density. So, the light scattering intensity per volume, I , is proportional to $(\nabla \cdot \mathbf{u})^2$ for the acoustic branch, and proportional to the average over the volume per particle, V_0 , of $(\nabla \cdot \mathbf{u}_f)^2$, where \mathbf{u}_f is the displacement vector for the high frequency mode. The proportionality constant is the same for both modes:

$$I_l \sim (\nabla \cdot \mathbf{u}_{ac})^2,$$

$$I_f \sim \frac{1}{V_0} \int_{V_0} (\nabla \cdot \mathbf{u}_f)^2 d^3r.$$

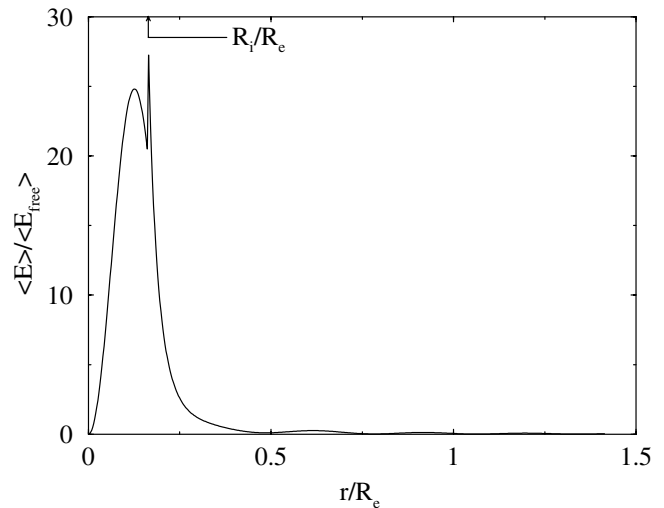


FIG. 4. The normalized energy density distribution for the d ($\ell = 2$) resonance mode at 6.0 GHz.

The ratio, $(I_l/I_f)_{\text{th}} \approx 14.4$, is in reasonable agreement with the experimental one $[(I_l/I_f)_{\text{exp}} \approx 12]$, as deduced from the middle panel of Fig. 1.

Finally, we included in our calculations the effects of absorption by replacing in the coating region the ω/c by $\omega/c + ia\omega^2$. The coefficient a includes the contributions of viscosity and thermal conduction [15]. We found that $a\omega^2/(\omega/c) = a\omega \approx 0.03$ (at the resonance) and that the position and the half width of the resonance did not change appreciably, although its height was reduced.

In conclusion, high resolution Brillouin scattering has shown that soft colloidal particles exhibit unexpected acoustic excitations at low volume fractions. We have developed a theoretical model that explains the nature of the opticlike mode, in good agreement with the experimental frequency, its local character, as well as the intensity of the inelastic light scattering. These limited results suggest that Brillouin scattering might be useful for dynamic characterization of functional biological assemblies.

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