Acoustic properties of colloidal crystals

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We present a systematic study of the frequency band structure of acoustic waves in crystals consisting of nonoverlapping solid spheres in a fluid. We consider colloidal crystals consisting of polystyrene spheres in water, and an opal consisting of close-packed silica spheres in air. The opal exhibits an omnidirectional frequency gap of considerable width; the colloidal crystals do not. The physical origin of the bands are discussed for each case in some detail. We present also results on the transmittance of finite slabs of the above crystals.

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I. INTRODUCTION

Colloidal suspensions of monodisperse spherical particles, with a diameter between 1 nm and 1 µm, in liquids or gases self assemble onto three-dimensional simple lattices whose lattice parameter can be easily tailored, providing new opportunities for fundamental as well as for applied research (see, e.g., Ref. 1 and references therein). The optical properties of these colloidal crystals are being investigated by many research groups because they seem to be good photonic band-gap materials, but they have interesting acoustic properties as well. Moreover, experiments relating to the reflection, transmission and absorption of ultrasonic waves by colloidal crystals can be very useful for the characterization of such systems, provided the means exist for a proper theoretical analysis of the experimental data. Finally, theoretical results for colloidal crystals offer a starting point for the understanding, at a semiquantitative level, of the propagation of acoustic waves in corresponding random media consisting of monodispersed spherical particles in a fluid.

The vibration modes (normal modes of the elastic field) of a phononic crystal, by which we mean a composite material whose density ρ(r) and Lamé coefficients λ(r) and μ(r) vary periodically in space, are Bloch waves with a corresponding frequency band structure which is analogous to that of electrons in ordinary crystals and electromagnetic waves in photonic crystals.1 With an appropriate choice of the parameters involved one may obtain phononic crystals with absolute (omnidirectional) frequency gaps (phononic gaps) in selected regions of frequency. An elastic wave, whose frequency lies within an absolute frequency gap of a phononic crystal, incident on a slab of the crystal of certain thickness will be reflected by it, the slab operating as a perfect nonabsorbing reflector of elastic waves in the frequency region of the gap.2 It may be possible, for example, to construct in this way vibration-free cavities which might be very useful in high-precision mechanical systems operating in a given frequency range.

In this paper we investigate in detail the acoustic properties of fcc colloidal crystals of polystyrene spheres in water and of close-packed silica spheres in air (opals). Given that these systems have a characteristic length scale of the order of 1 µm, they should exhibit interesting acoustic properties at ultrasonic frequencies of a few hundred MHz to a few GHz. It should be noted, however, that our results apply to different regions of frequency of the acoustic field provided that the size of the spheres and of the unit cell are scaled accordingly, and provided the elastic coefficients can be taken as constants independent of frequency over the said regions. The calculations of the frequency band structure and of the transmission coefficient of acoustic waves through a slab of the material were done using the layer-multiple-scattering formalism we have developed for this purpose.11 A formalism along the same lines has also been published by Liu et al.12 We have already demonstrated the efficiency of this method...
in relation to solid-solid composites. The present paper shows that the method applies equally well to phononic crystals consisting of nonoverlapping solid spheres in a fluid host; it appears that the plane-wave method for calculating the frequency band structure of such systems has convergence problems. Besides, we shall pay particular attention to the physical origin of the different modes of the acoustic field in the systems under consideration.

II. POLYSTYRENE SPHERES IN WATER

We consider a model colloidal crystal consisting of polystyrene spheres in water. The mass density and the sound velocities for polystyrene are: \( \rho_p = 1050 \text{ kg/m}^3 \), \( c_{tp} = 2400 \text{ m/s} \), and \( c_{tp} = 1150 \text{ m/s} \). For water we have: \( \rho_w = 1000 \text{ kg/m}^3 \), \( c_w = 1480 \text{ m/s} \). We begin by considering the scattering of a harmonic plane acoustic wave (a longitudinal wave) at an angular frequency \( \omega \), by a single polystyrene sphere of radius \( S \) in water; the water extends over all space. The incident plane wave can be written as a sum of spherical waves associated with the spherical harmonics \( Y_{lm} \), where \( l = 0, 1, 2, \ldots \) and \( m = -l, \ldots, 0, \ldots, l \), as usual. A spherical wave of given \((l,m)\) scatters independently of the others, of different \((l,m)\), because of the spherical symmetry of the scatterer; therefore the total scattering cross section is the sum of partial \((l,m)\) cross sections, with \( l \) up to a maximum \( l_{\text{max}} \) depending on the size parameter, \( \omega S/c_w \), of the sphere. We assume that waves with \( l > l_{\text{max}} \) do not scatter from the sphere and do not contribute to the total scattering cross section. Of course partial cross sections of different \( m \) (but of the same \( l \)) are equal because of the spherical symmetry of the system. In Fig. 4 we show the total scattering cross section for a plane wave scattered by a polystyrene sphere in water as a function of \( \omega S/c_w \). The peaks correspond to resonant modes of the acoustic field about the sphere with an angular distribution of the displacement field at the surface of the sphere determined by the spherical waves which contribute to these modes. We find that the resonance at \( \omega S/c_w = 1.49 \) is an \( l = 2 \) resonance: the displacement field associated with it is made up almost entirely (98%) from \( l = 2 \) spherical waves; the one at \( \omega S/c_w = 2.19 \) is an \( l = 3 \) resonance: the corresponding displacement field is made up mostly (90%) from \( l = 3 \) spherical waves; finally the field associated with the resonance at \( \omega S/c_w = 2.83 \) is made up mostly from \( l = 4 \) waves (65%) and \( l = 1 \) waves (22%). And we remember that there will be \((2l+1)\) resonant modes of the displacement field corresponding to \( m = -l, \ldots, 0, \ldots, l \) of the same frequency \( \omega_l \), i.e. \( \omega_l \) is \((2l+1)\)-degenerate.

We now consider a fcc crystal, with lattice constant \( a \), of nonoverlapping polystyrene spheres in water. We view the crystal as a sequence of \((111)\) planes of spheres. The spheres of a plane are arranged on a hexagonal lattice of lattice constant \( a_0 = a\sqrt{2}/2 \), defined by the primitive vectors \( \mathbf{a}_1 = a_0(1,0) \) and \( \mathbf{a}_2 = a_0(1/2, \sqrt{3}/2) \), in the \( xy \) plane (plane of the spheres). The \((n+1)\)th plane along the \( z \) axis is obtained from the \( n \)th plane by a primitive translation, \( \mathbf{a}_3 \), of the crystal. The planes are separated along the \( z \) direction by a distance \( d = a\sqrt{3}/3 \).

Fig. 3(a) shows the frequency band structure of acoustic waves in this crystal normal to the \((111)\) surface, obtained by the method of Ref. 11, when the fractional volume occupied by the spheres is \( f = 30\% \). In this case, the component of the reduced wavevector within the surface Brillouin zone (SBZ) of the fcc \((111)\) surface, \( \mathbf{k}_\parallel \),
We see that the frequency bands of Fig. 2(a) appear in
group associated with this point, as shown in Fig. 2(a).
Γ point (corresponding frequency bands are doubly
degenerate. At the non-degenerate, and Λ field belong to the irreducible representations of the
Og where a responding to the lattice defined by
where it practically vanishes, and this includes regions of
multiple scattering between the surfaces of the slab; else-
habits the well-known Fabry-Perot-like oscillations due to
scattering between the surfaces of the slab; elsewhere
practically vanishes, and this includes regions of
frequency where only bands of the Λ2 and/or Λ3 symmetry
exist. Of course the above argument holds for normal
incidence; off this direction the symmetry argument does
not apply, and there will be some transmission if there
are any propagating modes of the acoustic field at the
given frequency (see below, Fig. 3).

From a practical point of view, once the frequency
band structure and, if required, the transmission coef-
ficient have been calculated, one has all that is necessary
for a comparison with relevant experimental data. How-
ever, it is worthwhile to look at the physics behind the
band structure of Fig. 2. We note that the five narrow
bands about ω/cw = 1.5 (we remember that the Λ3
band is doubly degenerate) derive from the l = 2 reso-
nances on the individual spheres, which interact weakly
between them. The five-fold degeneracy of the reso-
nance of the single sphere is split by this interaction
in accordance with the lower (cubic) symmetry of the
crystal field. Similarly, the seven narrow bands about
ω/cw = 2.2 derive from the l = 3 resonances on the
individual spheres. We observe the small hybridization gaps

\[ u(\omega; k) = \sum_{\mathbf{g}} \left\{ u_{g}^{+} \exp \left[ i \mathbf{K}_{g}^{+} \cdot (\mathbf{r} - \mathbf{A}_n) \right] + u_{g}^{-} \exp \left[ i \mathbf{K}_{g}^{-} \cdot (\mathbf{r} - \mathbf{A}_n) \right] \right\}, \]

(1)

with

\[ \mathbf{K}_{g}^{\pm} = \left( k_{||} + g_{||} \pm \left[ \left( \omega/c_{w} \right)^{2} - (k_{||} + g_{||})^{2} \right]^{1/2} \right), \]

(2)

where g are the two-dimensional reciprocal vectors cor-
responding to the lattice defined by \(\mathbf{a}_1\) and \(\mathbf{a}_2\) above, and \(\mathbf{A}_n\) is a point between the nth and \((n+1)\)th planes. A
generalized Bloch wave satisfies the equation

\[ u_{g_{n+1}}^{+} = \exp (i \mathbf{k} \cdot \mathbf{a}_3) u_{g_{n}}^{+}, \]

(3)

where \(\mathbf{a}_3 = \mathbf{A}_{n+1} - \mathbf{A}_n\) and \(\mathbf{k} = (k_{||}, k_{z}(\omega; \mathbf{k}_{||}))\). We note
that, although both longitudinal and transverse modes of
the elastic field are considered within the (solid) spheres,
only longitudinal modes exist in the (fluid) host region
in the absence of viscosity. Therefore, in a binary com-
posite of nonoverlapping solid spheres in a fluid host,
where the solid component does not form a continuous
network, there cannot be propagating transverse waves.

Consequently, at the Γ point \((k_{||} = 0, k_{z} = 0)\) the disper-
sion curves [Fig. 2(a) and also Figs. 2(b), 2(c), and 2(a) below], show only one (longitudinal) branch starting from zero
frequency, instead of the three (corresponding to both
longitudinal and transverse modes) appearing in solid-
solid composites.

One can easily show that when \(k_{||} = 0\), the \(g = 0\)
component of the wavefield, described by Eq. (1), van-
nishes \((u_{g=0}^{+} = 0)\) for the modes of the Λ2 or the Λ3
symmetry; only the Λ1 symmetry allows a non-vanishing
\(g = 0\) component of the wavefield. Now assume that we
have a slab of the crystal of finite thickness, i.e., N fcc
(111) planes of polystyrene spheres; between the spheres
and to the left and right of the slab, extending to infin-
ity, we have water. There, and for the frequency range
which interests us here, the acoustic wavefield has only
the one component \(g = 0\). And therefore the external
field couples with the field inside the slab essentially only
pairs: \(k_{z}(\omega; \mathbf{k}_{||} = 0), -k_{z}(\omega; \mathbf{k}_{||} = 0)\). However, this
symmetry property is not valid for an arbitrary value of
\(\mathbf{k}_{||}\), because the crystal under consideration, described by
the \(O_\text{h}\) group, does not have a plane of mirror symme-
try parallel to the (111) surface which would transform
\((k_{x}, k_{y}, k_{z})\) to \((k_{y}, k_{y}, -k_{z})\). The above symmetry prop-
erty holds only for \(k_{||}\) on the x axis \([\mathbf{k}_{||} = (k_{x}, 0)\],

The (longitudinal) wavefield, of given \(\omega\) and \(\mathbf{k}_{||}\), in the
host region between the nth and the \((n+1)\)th planes of
spheres, can be expanded into plane waves propagating
(or decaying) to the left and to the right as follows

\[ u_{g_{n+1}}^{+} = \exp (i \mathbf{k} \cdot \mathbf{a}_3) u_{g_{n}}^{+}, \]
opening up about $\omega S/c_w \approx 1.5$ and about $\omega S/c_w \approx 2.2$, between bands of the same symmetry.

There is also a mode of propagation of acoustic waves corresponding to almost free propagation in an effective homogeneous medium. In the absence of the resonances associated with the spheres, this mode of propagation, which has the $\Lambda_1$ symmetry, would dominate the frequency band structure of the acoustic field as shown in Fig. 3(a). It was calculated by suppressing the $l > 1$ resonances, i.e. cutting off the $l > 1$ spherical waves, which give rise to these resonances, from the spherical-wave expansion of the wavefield (see Ref. [3]). In the long-wavelength limit ($\omega \to 0$) we obtain a linear dispersion curve, the slope of which gives an effective velocity of sound for the composite medium, $\bar{c} = 1589$ m/s, which is in very good agreement with the result $\bar{c} = 1566$ m/s, of the effective-medium approximation. The small gap about $\omega S/c_w \approx 1.5$ in Fig. 3(a), is a Bragg gap; it is analogous to the small gaps one obtains at the edges of the Brillouin zone in the electronic band structure of free-electron-like metals. When the resonances on the spheres are allowed in, one obtains the band structure shown in Fig. 3(b), with apparent hybridization gaps between the continuum band [of Fig. 3(a)] and resonance bands of the same symmetry ($\Lambda_1$).

We believe that the disorder that is naturally there in a colloidal solution, does not eradicate the essential characteristics of the acoustic modes as calculated here, which are determined by the local environment about a sphere and less so by long range order. We would expect the fine features associated with narrow bands to be smoothed out by disorder, but bands of modes separated by gaps could remain. This would be in accordance with the results of Brillouin-scattering experiments on disordered colloidal suspensions of monodispersed polymethylmethacrylate (PMMA) spheres in transparent oil. It has been shown that in these colloidal suspensions different longitudinal modes of propagation of the acoustic field exist which are separated by frequency gaps about the resonance frequencies of an individual PMMA sphere, which agrees, at a semiquantitative level, with the hybridization-induced gaps discussed above.

In Fig. 4(a) we show an example of the band structure for a $k_{||} \neq 0$, and next to it, in Fig. 4(b), the transmission coefficient of an acoustic wave, with the same $k_{||}$, incident on a slab of the material consisting of 32 fcc (111) planes of polystyrene spheres. The thing to note is that all bands are active in this case, although the transmission coefficient is not always unity [compare with Fig. 3(a)]. We remember that the incident wave cannot have a frequency smaller than $\omega_{\text{ini}}f = c_w |k_{||}|$. Finally, it can be seen that now the frequency bands do not have the reflection symmetry found in the case of $k_{||} = 0$ [Fig. 3(a)], for the reasons given above.

We calculated the frequency band structure for a sufficient number of $k_{||}$ points within the SBZ. There is a near-omnidirectional gap about $\omega S/c_w \approx 1.3$; we tried to turn this gap into a proper omnidirectional gap by changing some of the parameters, but we did not succeed.

In Fig. 5 we look at the dependence of the frequency band structure on the fractional volume occupied by the spheres. We see in particular that the width of the resonance bands increases with $f$, apparently because the spatial overlap of the wavefield associated with resonances on neighboring spheres increases with $f$.

III. OPALS

In this section we consider a phononic crystal, an artificial opal, consisting of two media (silica spheres in air) with density and velocity contrasts much higher than was the case in the crystal (polystyrene spheres in water) studied in the preceding section. Opalescent structures
(usually referred to as synthetic or artificial opals) can be obtained from monodispersed silica colloids, e.g. by sedimentation in the gravitational field. In this way, fcc arrays of silica microspheres in air, near the close-packing density ($\phi \approx 74\%$), similar to a natural opal, have been obtained. Here we present some results on the acoustic properties of such an opal. The mass density and sound velocities for silica are: $\rho_s = 2200 \text{ kg/m}^3$, $c_{ts} = 5970 \text{ m/s}$, $c_{ls} = 3760 \text{ m/s}$. For air we have: $\rho_a = 1.23 \text{ kg/m}^3$, $c_a = 340 \text{ m/s}$.

Proceeding as in Section II, we first consider the scattering of a harmonic plane acoustic wave, of angular frequency $\omega$, by a single silica sphere of radius $a$ in air. In this case the total scattering cross section is a slowly increasing function of $\omega S/c_a$ (see Fig. 6). However, the partial cross sections, corresponding to different values of $l$, exhibit well defined resonance peaks, of some width, as can be seen from Fig. 6. At $\omega S/c_a = 2.22$ we obtain an $l = 0$ resonance, at $\omega S/c_a = 3.88$ an $l = 1$ resonance, and at $\omega S/c_a = 5.25$ an $l = 2$ resonance.

We consider then an fcc crystal of nonoverlapping silica spheres in air with $f = 74\%$ and view it as a sequence of (111) planes of spheres. Fig. 3(a) shows the frequency band structure of the infinite crystal, for $k_0 = 0$. The physical origin of the bands shown in Fig. 3(a), other than the flat band about $\omega S/c_a = 3.426$, can be understood in much the same way as for the bands of Fig. 3(a). In the absence of hybridization we would have, extending practically over the entire frequency range, a mode corresponding to almost free propagation in an effective homogeneous medium, with Bragg gaps opening up at $\omega S/c_a \approx 1.5$ at the edges of the Brillouin zone and about $\omega S/c_a \approx 3.5$ at the center of the Brillouin zone; and we would have also resonance bands developing about the $l = 0$ and $l = 1$ resonances of the individual spheres. From Fig. 3 we expect a single $l = 0$ resonance band of $A_1$ symmetry about $\omega S/c_a \approx 2.2$; and three $l = 1$ bands about $\omega S/c_a \approx 3.9$, of which one should be non-degenerate ($A_1$ symmetry) and one doubly degenerate ($A_3$ symmetry). We expect a degree of hybridization between bands of the same ($A_1$) symmetry, and this naturally leads to the bands shown in Fig. 3(a), except for the one flat band, a doubly degenerate band of $A_3$ symmetry, about $\omega S/c_a = 3.426$, which appears to have a very different physical origin (see below).

In the long-wavelength limit ($\omega \to 0$) we obtain a linear dispersion curve, the slope of which gives an effective velocity of sound in the composite medium, $\bar{c} = 278 \text{ m/s}$, which is in very good agreement with result $\bar{c} = 291 \text{ m/s}$ of the effective-medium approximation. We note that this agreement is greatly improved at lower values of the volume-filling fraction $f$. It is worth noting, also, that the effective velocity of sound in a system of silica spheres in air is smaller than in air because of the high density contrast between silica and air. Indeed, in the limit $\rho_a << \rho_s$, the effective-medium approximation gives practically identical results with the simple expression $\bar{c}/c_a = [2/(2 + f)]^{1/2}$, which gives $\bar{c} < c_a$ at any value of $f$.

It seems that the modes corresponding to the flat band about $\omega S/c_a = 3.426$, which are deaf modes, are those of a wavefield highly concentrated between consecutive planes of spheres, with very little interaction between neighbor regions of high concentration. In order to demonstrate the above, we looked for the eigenmodes of the acoustic field, for $k_0 = 0$, in a slab of $N = 2, 4, 8, 16$ planes of spheres, in the manner described for the corresponding problem of the electromagnetic field, over a frequency range about the said flat band of Fig. 3(a). Because of the two-dimensional translation symmetry of the slab, the wavefield, in the air regions, can be expanded as in Eq. (1) in a series of plane waves with wavevec-
The doubly degenerate eigenfrequencies of the corresponding bound states in slabs of spheres are noted by circles. The doubly degenerate eigenfrequencies of the finite crystal consisting of 32 planes of spheres. We can see experimentally this band. The corresponding modes do not couple to an incident wave. This is demonstrated quite clearly in Fig. 8(b), which shows the transmission coefficient of a wave incident normally on a slab of the material consisting of 32 planes of spheres. We can see that the transmission coefficient vanishes at and about \( \omega S/c_a = 3.426 \) where the band under consideration exists. However, we have verified that the said band survives for \( k_\parallel \neq 0 \) (at least in the neighborhood of \( k_\parallel = 0 \)) where it couples with an incident wave of the same \( k_\parallel \) leading to measurable transmittance.

In Fig. 9, we present the projection of the frequency band structure of the acoustic field of the phononic crystal under consideration, on the symmetry lines of the SBZ of the fcc (111) surface. The shaded regions extend over the frequency bands of the acoustic field: at any one frequency within a shaded region, for a given \( k_\parallel \), there exists at least one propagating acoustic mode in the infinite crystal. The blank areas correspond to frequency gaps. We note that knowing the modes with \( k_\parallel \) in the shaded area (\( \Gamma \bar{K} \bar{M} \)) of the SBZ and \(-\pi/d < k_\parallel \leq \pi/d \) is sufficient for a complete description of all the modes in the infinite crystal. The modes in the remaining of the reduced \( k \) space are obtained through symmetry. One clearly sees that for the opal under consideration, and unlike the colloidal crystal studied in Section 4, one obtains an omnidirectional frequency gap extending from \( \omega S/c_a = 1.59 \) to \( \omega S/c_a = 1.95 \). We verified that this is indeed so by calculating the band structure at a sufficient number of \( k_\parallel \) points in the SBZ. Finally, we should note the existence of a very narrow omnidirectional gap at higher frequencies, extending from \( \omega S/c_a = 3.30 \) to \( \omega S/c_a = 3.34 \).

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