Anomalous waveforms observed in laboratory-formed gas hydrate-bearing and ice-bearing sediments

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Acoustic transmission measurements of compressional, P, and shear, S, wave velocities rely on correctly identifying the P- and S-body wave arrivals in the measured waveform. In cylindrical samples for which the sample is much longer than the acoustic wavelength, these body waves can be obscured by high-amplitude waveform features arriving just after the relatively small-amplitude P-body wave. In this study, a normal mode approach is used to analyze this type of waveform, observed in sediment containing gas hydrate or ice. This analysis extends an existing normal-mode waveform propagation theory by including the effects of the confining medium surrounding the sample, and provides guidelines for estimating S-wave velocities from waveforms containing multiple large-amplitude arrivals. [DOI: 10.1121/1.3552877]

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I. INTRODUCTION

Compressional, P, and shear, S, wave velocity measurements are routinely used to remotely investigate physical properties of man-made or naturally occurring materials (ASTM, 2005; Zhou *et al.*, 2009), including the Earth itself (Aki and Richards, 1980). In granular material, P-, to a greater extent, and S-wave velocities can be used to investigate the strength of intergranular contacts (Santamarina *et al.*, 2001).

Gas hydrate-bearing sediment (GHBS) is an example of a naturally occurring material that has been investigated using P- and S- wave velocity measurements in both the natural environment and in the laboratory. Gas hydrates are clathrates, crystalline solids comprised of guest molecules, primarily methane in nature, encaged in a water-molecule lattice. Gas hydrates are stable at the high pressures and relatively low temperatures which present in ocean-margin and permafrost sediments (Kvenvolden and Lorenson, 2001), and occur in such abundance as to attract interest as a potential energy resource (Boswell, 2009), geohazard (McIver, 1982), and a climate change agent (Archer, 2007).

Laboratory studies of GHBS carried out with the Gas Hydrate And Sediment Test Laboratory Instrument (GHAS-TLI) (Winters *et al.*, 2000) utilize cylindrical samples that are twice as long as they are wide. Whereas this aspect of ratio follows standard guidelines for triaxial shear strength measurements (ASTM, 2004), the sample geometry results in waveforms with large-amplitude features trailing the P-wave arrival and preceding the S-wave arrival. These large-amplitude features can obscure, or be mistaken for, the S-body wave arrival. To reliably obtain P- and S-wave

velocities from waveforms under these conditions require a theoretical structure for identifying waveform features in the high-frequency case for which the acoustic wavelength is much smaller than the sample length.

Wave propagation in cylinders has been extensively analyzed by Kolsky (1963), Mirsky (1965), Graff (1975), and others (Honarvar *et al.*, 2007, and references therein), but these low-frequency analyses are not appropriate for the high-frequency case discussed here. At high frequencies, when a sample has sufficient length for acoustic energy traversing the sample to undergo numerous internal reflections, some of the reflected waves can constructively interfere, propagating as energy packets called normal modes (Grant and West, 1965; Rinehart, 1975). Because normal modes are generated by internal reflections; their type, velocity, and amplitude all depend on the sample's geometry, internal structure, and properties of the material surrounding the sample. Like P- and S-body waves, normal-mode propagation also depends on the sample's intrinsic elastic properties.

Based on the dependence of the velocity on frequency for the large-amplitude features observed in the gas hydrate-bearing and ice-bearing sediments, a normal-mode solution has been derived and verified with waveforms generated in aluminum cylinders by P-wave (Lee and Waite, 2009) and S-wave transducers (Lee and Waite, 2010). Here we extend the normal-mode theory to account for confining fluid around a sample and apply our theoretical approach to waveforms measured in gas hydrate- or ice-bearing sand samples. We illustrate how the normal-mode approach can be used to estimate the S-wave velocity in the case where the S-body wave is obscured by a normal-mode feature. Additionally, these laboratory samples are briefly destabilized causing the gas hydrate or ice to migrate within the sample. The normal-mode type and location in the waveform vary dramatically in response to these changes in the sample's internal

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structure, providing a test of the normal mode approach's capacity to consistently identify large-amplitude waveform features.

II. EXPERIMENT

A. Measurement apparatus

GHASTLI is a triaxial-strength-measurement device that tests cylindrical samples typically 140 mm long and 70 mm in diameter [Fig. 1(A)]. The cylindrical sample is capped at each end by a titanium endcap in which P- and S-wave piezoelectric crystals are housed behind a wear plate [Fig. 1(B)]. The center frequency of each crystal is 1 MHz. Flow lines into each endcap allow either gas or water in and out of the sample, and a heat exchanger [Fig. 1(A)] allows temperature control of the sample.

Once a sample has been prepared and mounted as shown in Fig. 1(A), the sample stage is lifted into the pressure vessel, visible at the top of Fig. 1(A), and sealed with a gasket. The chamber is then filled with silicone oil that is subsequently pressurized to provide a confining stress. An axially aligned piston penetrating the top of the pressure chamber contacts the heat exchanger to provide an axial load for sample deformation and to monitor the sample length. Additional apparatus details are available in [Winters *et al.* \(2000\)](#) and [Waite *et al.* \(2008, 2004\)](#).

Acoustic waveforms are generated with a Panametrics Model 5800 Pulser/Receiver (Waltham, MA), exciting either the P- or S-wave crystal in one endcap. The signal traverses the sample and is received by the corresponding crystal in the opposing endcap. The signal is displayed on a Tektronix TDS-340 oscilloscope (Beaverton, OR) and stored to disk. Wave velocity is calculated by dividing the sample length by the arrival time of a given waveform feature. To account for the time required for the signal to propagate through the electronics and endcaps rather than the sample, the arrival time is corrected by subtracting the arrival time when the endcaps are in head-to-head contact with no sample ([Waite *et al.*, 2008](#)). Both an S- and smaller precursor P-waves are transmitted when the S-wave crystal in either endcaps are excited, providing a means of obtaining simultaneous P- and S-wave velocity measurements using a single waveform ([Ayling *et al.*, 1995](#); [Helgerud *et al.*, 2009](#)). The P-wave crystals produce a higher amplitude P-wave and can be used if the precursor P-wave is not observable when using the S-wave crystals.

B. Sample preparation

The samples discussed here are formed initially by pre-mixing deionized water with Ottawa sand sieved to obtain the 250–500 μm grain-size fraction. The added water volume is chosen to obtain the desired saturation of gas hydrate or ice, assuming complete conversion of the water. The final pore-space saturations are given in Table I. The water and sand mixture is tamped into a cylindrical viton membrane that is wired to one endcap. The second endcap is wired onto the opposite end after tamping is complete. Mass and

FIG. 1. (Color online) (A) A sample ready to be raised into the main chamber of the GHASTLI. The 140-mm-long sample is jacketed in a flexible latex or viton membrane. (B) Each endcap contains a disc-shaped S-wave transducer crystal surrounded by a doughnut-shaped P-wave transducer crystal, shown schematically as they are positioned behind the wear plate, which contacts the sample. The shear crystal is 6 mm in diameter and the P-wave crystal outer diameter is 9 mm. The endcap and sample diameter is 70 mm.

volume measurements show this procedure results in samples with $\sim 38\%$ porosity.

To form GHBS, the sand and water mixture is pressurized and held at 12 MPa pore pressure with methane gas and 12.25 MPa confining pressure with silicone oil in GHASTLI. Once the pore pressure and the 0.25 MPa effective pressure are set, the sample is cooled to 6°C. Water and gas in the sample combine to form methane hydrate, cementing the

TABLE I. Velocities of GHBS and IBS at a given pore-space saturation of hydrate or ice. α_1 , β_1 , G_α , are the P-wave, S-wave, and normal-mode group velocities of GHBS and IBS. F_d is the dominant frequency of the normal mode. Normal modes are denoted as nondispersive normal modes (NDNM), or second order normal modes (Second). Pre- and post-depressurization/repressurization cycle (D/R) results are given to indicate the impact of a D/R cycle on the observed waveform.

Pore-space content	α_1 (km/s)	β_1 (km/s)	G_α (km/s)	F_d (MHz)	Type of normal mode	Remarks
20% GHBS	2.83	1.58	2.35	0.25	NDNM	Pre-D/R
43% GHBS	3.51	1.90				Pre-D/R
20% GHBS	2.96	1.77	2.73	0.33	Second	Post-D/R
43% GHBS	3.44	1.95	2.87	0.28	NDNM	Post-D/R
43% GHBS ^a	3.67	2.21	3.42	0.48	Second	Post-D/R
18% IBS	3.25	1.96	2.80	0.32	NDNM	Pre-D/R
34% IBS	3.56	2.18	3.07	0.34	NDNM	Pre-D/R
65% IBS	4.16	2.51	3.54	0.45	NDNM	Pre-D/R
34% IBS	3.61	2.21	3.10	0.41	NDNM	Post-D/R

^aMeasurement was made in 2007 with new endcaps and transducers. All other measurements were made in 2006 with an older transducer/endcap pair.

sediment grains and thereby increasing both the observed wave velocity and amplitude (Waite *et al.*, 2004). Hydrate formation is deemed complete when the waveform amplitude and velocity stabilize. From the onset of hydrate formation, it takes 5 days to reach 20% pore-space gas hydrate saturation and 14 days for 43% saturation. The hydrate saturation is determined at the end of each test by warming the sample to dissociate the hydrate. The pore volume change, as recorded by the pore pressure pump as it maintains a constant pore pressure in the sample, is used to calculate the sample's hydrate content using the technique described by Waite *et al.* (2004).

For ice-bearing sediment (IBS), the sand and water mixture, enclosed within the viton membrane and endcaps, is clamped with a C-clamp to ensure continued contact between the endcaps and sample during freezing. The sample and C-clamp are stored in a chest freezer at -25°C overnight before waveforms are measured. These samples are surrounded by air with no additional confining or pore pressure. As with GHBS, ice forming from the water cements sand grains resulting in waveform features with high velocities and amplitudes.

The GHBS samples described here were destabilized as part of a study reported by Waite *et al.* (2008) that included X-ray computed tomography (CT) imagery, thermal and mechanical property measurements, including P- and S-wave velocities. Understanding the impact of a brief destabilization on GHBS is important because field studies of GHBS now use pressure coring systems capable of obtaining GHBS while maintaining the *in situ* pressure (Expedition 311 Scientists, 2006; Leg 204 Shipboard Scientific Party, 2003). To make triaxial strength measurements or transport the GHBS, however, the pressurized core must be briefly depressurized to room pressure, cut to length, then repressurized either in a test apparatus or in a storage chamber (Collett *et al.*, 2006; Expedition 311 Scientists, 2006). This process lasts approximately for 5 min (P. Schultheiss, personal communication, 2007), altering the sample's properties and obscuring the connection between laboratory-measured properties and the original *in situ* property values.

To estimate the extent to which structural changes occur as a result of briefly destabilizing GHBS in this fashion, the

depressurization/repressurization cycle is simulated in GHASTLI by dropping both the pore and confining pressures to atmospheric conditions, then repressurizing the sample. The sample is allowed to re-equilibrate at 6°C , with 12 MPa methane pore pressure and 12.25 MPa silicone oil confining pressure. The samples are out of the hydrate stability field for 7–8 min during this process. Because gas hydrate persists in the sample interior (Waite *et al.*, 2008), hydrate reforms rapidly migrating toward the sample's central axis. The waveforms stabilize in 2 days for the 20% saturation sample, and 3 days for the 43% saturation sample. Because the hydrate migrates during this process, however, the sample's internal structure and measured properties before and after the brief depressurization differ.

For the IBS, samples are removed from the freezer and allowed to warm for 5 min beyond the time at which melting begins to alter the measured waveform. This mimics the 5-min destabilization that GHBS endures during a pressure vessel transfer in the field. The IBS sample is then returned to the freezer overnight before obtaining a waveform characteristic of the restabilized sample.

C. Evidence of normal modes in measured waveforms for GHBS

S-wave crystals are used to obtain waveforms in samples with 20% and 43% of their pore space saturated with gas hydrate [Figs. 2(A) and 2(B), respectively]. The solid waveforms are measured after hydrate formation is complete, but prior to briefly destabilizing the sample. The dotted waveforms are measured after the sample has re-equilibrated following the brief depressurization and subsequent repressurization, referred to as the D/R cycle. As noted in Sec. II B and discussed in Sec. V A, the hydrate migrates toward the sample's central axis during the D/R cycle (Waite *et al.*, 2008). This alters the radial density profile which in turn alters the waveform features. To obtain the correct P- and S-wave velocities through such a sample requires a tool for identifying the observed large-amplitude waveform features.

The P-wave can be identified as the first arrival in each waveform, as indicated by the solid circles in Fig. 2. Without

FIG. 2. (Color online) Waveforms measured using shear transducers before and after a brief destabilization of the GHBS; denoted pre- and post-D/R cycle, respectively. (A) Waveforms for Ottawa sand with 20% of the pore space saturated with hydrate. (B) Waveforms for Ottawa sand with 43% pore-space hydrate saturation. The solid circle in each plot represents the first arrival, a P-wave. Arrows indicate the first peak in the normal mode immediately following the P-wave. Normal-mode velocities are calculated from their first arrivals, not the peak positions indicated by the arrows. For 43% pre-D/R GHBS (solid curve), the peaks and troughs ahead of the S-wave are fairly uniform. Because there is no discernible, isolated large-amplitude feature arriving before the S-wave, no normal mode is indicated in Fig. 2(B).

additional insight, however, it is not readily obvious which of the subsequent large-amplitude features represents the S-wave. We propose the large-amplitude feature that closely follows the P-wave arrival is a normal mode, but there are two other possibilities to consider: The arrival could be either an S-wave or a P-wave that has reflected off the sample's cylindrical surface at some point along the sample length.

Considering the post-D/R waveforms, the large amplitude arrives with 95% of the P-wave velocity in the 20% saturation case [Fig. 2(A)] and 83% of the P-wave velocity in the 43% saturation case. In contrast, the S-wave speed in hydrate-bearing sediment is expected to be less than $\sim 60\%$ of the P-wave speed (Lee, 2002; Matsushima, 2006; Yun *et al.*, 2005), even if the hydrate is cementing the sediment grains (Priest *et al.*, 2005). Therefore, the large-amplitude arrival immediately following the P-wave is too fast to be an S-wave.

The large-amplitude feature also cannot be a P-wave reflection off the cylindrical sample boundary, given the calculated expected arrival time of such a feature. In the 20% saturation sample [Fig. 2(A)], the sample length after the D/R cycle is 12.92 mm and the sample radius is assumed to be constant at its initial value of 35 mm. To reflect off the cylindrical surface midway along the sample length, the P-wave must travel 146.9 mm at 2.96 km/s (Table I), and would be expected to arrive at $49.6 \mu\text{s}$, or $\sim 3.7 \mu\text{s}$ after the observed arrival time of $45.91 \mu\text{s}$. In the 43% saturation case [Fig. 2(B)], the sample length after the D/R cycle is 132 mm; so for a sample radius of 35 mm, the path length for the reflected wave is 149.4 cm. At the P-wave velocity in that sample of 3.44 km/s (Table I), the reflected P-wave should arrive at $43.4 \mu\text{s}$, or $\sim 2.6 \mu\text{s}$ ahead of the observed arrival time of $46.01 \mu\text{s}$. In neither of the samples does the large-amplitude feature arrive at the time expected for a simple reflected P-wave, indicating that this feature is not likely to be a singly reflected P-wave.

The large-amplitude arrivals in Fig. 2 may instead result from the constructive combination of many internally reflected waves, some of which may have undergone a mode conversion from P- to S- or S- to P-waves in the process (Grant and West, 1965; Rinehart, 1975). These combined waves, or normal modes, exhibit two qualities observed in the high-amplitude features discussed above: (1) the normal-mode amplitude greatly exceeds the P-wave amplitude, which is expected given that P-wave amplitudes decay much more rapidly with sample length than do normal-mode amplitudes and (2) the dominant frequency of the normal mode scales with the velocity of the feature relative to the P-wave speed. This can be seen by comparing the large-amplitude feature in the 20% saturation case, which is both closer to the sample's P-wave speed and of higher frequency than its counterpart in the 43% saturation case. These observations are suggestive of normal-mode behavior, but to fully characterize these features requires a normal-mode wave propagation theory applicable to the high frequencies and long samples utilized in the experiments described here.

III. THEORY

The waveform features shown in Fig. 2 can be distinguished from one another based on a theoretical relation between each feature's dominant frequency and group velocity. In the context of normal modes, we establish this relation in three steps:

- (1) Derive a solution of the wave propagation equation for cylinders.
- (2) Derive the dispersion relation for that wave propagation equation to obtain the normal mode phase velocity dependence on frequency.
- (3) Derive, from that phase-velocity dependence on frequency, a high-frequency approximation from which we calculate the theoretical group velocity as a function of the waveform's measured dominant frequency.

We also derive expressions for the relative amplitudes of the normal modes, P- and S-body waves, then use these

predicted amplitude relations to confirm the frequency and velocity-based identification of the observed waveform features.

A. Wave equation solution

Under the assumption of axial symmetry, differential equations for wave propagation inside an infinitely long cylinder in a cylindrical coordinate system (r, θ, z) can be written as (e.g., Biot, 1952; Lee and Balch, 1982):

$$\frac{\partial^2 \Phi_i}{\partial r^2} + \frac{1}{r} \frac{\partial \Phi_i}{\partial r} + \frac{\partial^2 \Phi_i}{\partial z^2} = \frac{1}{\alpha_i^2} \frac{\partial^2 \Phi_i}{\partial t^2}, \quad (1a)$$

$$\frac{\partial^2 \Psi_i}{\partial r^2} + \frac{1}{r} \frac{\partial \Psi_i}{\partial r} - \frac{\Psi_i}{r^2} + \frac{\partial^2 \Psi_i}{\partial z^2} = \frac{1}{\beta_i^2} \frac{\partial^2 \Psi_i}{\partial t^2}, \quad (1b)$$

where Φ_i and Ψ_i are the scalar potentials for P- and S-waves in the i th medium, and α_i , β_i and t are the P-wave and the S-wave velocities in the i -th medium and time, respectively. Medium 1 represents the solid samples (GHBS or IBS) and medium 2 is the surrounding fluid (silicone oil for the GHBS, or air for the IBS). Given that (1) the surrounding medium is fluid, (2) there are no incoming waves in the fluid, (3) the P-wave source is located at the origin with a strength of V_0 , and (4) the S-wave source is located at the origin with a strength of S_0 , the formal solution of Eq. (1) in the frequency domain can be written as follows:

$$\begin{aligned} \Phi_1 &= \int A J_0(lr) e^{-ikz} dk + V_0 \int H_0^{(2)}(lr) e^{-ikz} dk, \\ \Psi_1 &= \int B J_1(mr) e^{-ikz} dk + S_0 \int H_1^{(2)}(mr) e^{-ikz} dk, \\ \Phi_2 &= \int C H_0^{(2)}(nr) e^{-ikz} dk, \end{aligned} \quad (2)$$

with

$$\begin{aligned} l &= \left(\frac{\omega^2}{\alpha_1^2} - k^2 \right)^{1/2} \text{ for } \omega/\alpha_1 > k \\ &= -i \operatorname{sgn} \omega \left(k^2 - \frac{\omega^2}{\alpha_1^2} \right) \text{ for } \omega/\alpha_1 < k, \\ m &= \left(\frac{\omega^2}{\beta_1^2} - k^2 \right)^{1/2} \text{ for } \omega/\beta_1 > k \\ &= -i \operatorname{sgn} \omega \left(k^2 - \frac{\omega^2}{\beta_1^2} \right) \text{ for } \omega/\beta_1 < k, \\ n &= \left(\frac{\omega^2}{\alpha_2^2} - k^2 \right)^{1/2} \text{ for } \omega/\alpha_2 > k \\ &= -i \operatorname{sgn} \omega \left(k^2 - \frac{\omega^2}{\alpha_2^2} \right) \text{ for } \omega/\alpha_2 < k, \text{ and} \\ k &= \omega/c, \end{aligned}$$

where ω is an angular frequency, c is the phase velocity, and J_n and $H_n^{(2)}$ are the Bessel functions of order n and the order n is the Hankel function of the second kind, respectively.

Note that uniformly expanding P- and S-wave sources are assumed.

Necessary boundary conditions to be satisfied for the solutions are:

- (1) Continuity of radial stress, p_r , i.e., $(p_{rr})_1 = (p_{rr})_2$.
- (2) Vanishing tangential stress, p_{rz} , i.e., $(p_{rz})_1 = (p_{rz})_2 = 0$.
- (3) Continuity of radial displacement, U_r , i.e., $(U_r)_1 = (U_r)_2$.

The radial and tangential stresses are given by:

$$\begin{aligned} (p_{rr})_i &= \lambda_i \left(\frac{\partial^2 \Phi_i}{\partial r^2} + \frac{1}{r} \frac{\partial \Phi_i}{\partial r} + \frac{\partial^2 \Phi_i}{\partial z^2} \right) + 2\mu_i \left(\frac{\partial^2 \Phi_i}{\partial r^2} - \frac{\partial^2 \Psi_i}{\partial r \partial z} \right) \\ &= -\lambda_i \frac{\omega^2 \Phi_i}{\alpha_i^2} + 2\mu_i \left(\frac{\partial^2 \Phi_i}{\partial r^2} - \frac{\partial^2 \Psi_i}{\partial r \partial z} \right), \end{aligned} \quad (3)$$

$$\begin{aligned} (p_{rz})_i &= \mu_i \left(2 \frac{\partial^2 \Phi_i}{\partial r \partial z} + \frac{\partial^2 \Psi_i}{\partial r^2} + \frac{1}{r} \frac{\partial \Psi_i}{\partial r} - \frac{\Psi_i}{r^2} - \frac{\partial^2 \Psi_i}{\partial z^2} \right) \\ &= \mu_i \left(2 \frac{\partial^2 \Phi_i}{\partial r \partial z} - \frac{\omega^2 \Psi_i}{\beta_i^2} - 2 \frac{\partial^2 \Psi_i}{\partial z^2} \right). \end{aligned} \quad (4)$$

Using Eqs. (2) and (4), continuity of radial stress yields:

$$\begin{aligned} (p_{rr})_1 &= -A \frac{\lambda_1 \omega^2}{\alpha_1^2} J_0(la) + 2\mu_1 A \left[\frac{l J_1(la)}{a} - l^2 J_0(la) \right] \\ &\quad + 2ik\mu_1 B \left[m J_0(ma) - \frac{J_1(ma)}{a} \right] \\ &\quad - V_0 \frac{\lambda_1 \omega^2}{\alpha_1^2} H_0^{(2)}(la) + 2V_0 \mu_1 \left[\frac{l H_1^{(2)}(la)}{a} \right. \\ &\quad \left. - l^2 H_0^{(2)}(la) \right] + 2ik\mu_1 S_0 \left[m H_0^{(2)}(ma) \right. \\ &\quad \left. - \frac{H_1^{(2)}(ma)}{a} \right] = (p_{rr})_2 = -C \frac{\lambda_2 \omega^2}{\alpha_2^2} H_0^{(2)}(na). \end{aligned} \quad (5)$$

Using Eqs. (2) and (4), vanishing tangential stress yields:

$$\begin{aligned} (p_{rz})_1 &= A 2ik\mu_1 l J_1(la) + V_0 2ik\mu_1 l H_1^{(2)}(la) \\ &\quad + B \left(2k^2 \mu_1 - \frac{\mu_1 \omega^2}{\beta_1^2} \right) J_1(ma) \\ &\quad + S_0 \left(2k^2 \mu_1 - \frac{\mu_1 \omega^2}{\beta_1^2} \right) H_1^{(2)}(ma) = 0. \end{aligned} \quad (6)$$

The radial displacement is given by:

$$(U_r)_i = \frac{\partial \Psi_i}{\partial r} - \frac{\partial \Phi_i}{\partial z}. \quad (7)$$

Using Eqs. (2) and (7), continuity of radial displacement yields:

$$\begin{aligned} (U_r)_1 &= -A l J_1(la) + B i k J_1(ma) - V_0 l H_1^{(2)}(la) + i k S_0 J_1(ma) \\ (U_r)_2 &= -C n H_1^{(2)}(na), \end{aligned} \quad (8)$$

Therefore, the boundary conditions satisfy the following matrix equation:

$$[Q] \equiv \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix}, \quad (9)$$

with

$$\begin{aligned} a_{11} &= lJ_1(la), \\ a_{12} &= -ikJ_1(ma), \\ a_{13} &= -nH_1^{(2)}(na), \\ a_{21} &= \rho_1(2k^2\beta_1^2 - \omega^2)J_0(la) + 2\rho_1\beta_1^2 lJ_1(la)/a, \\ a_{22} &= 2ik\mu_1 \left(mJ_0(ma) - \frac{J_1(ma)}{a} \right), \\ a_{23} &= \frac{\lambda_2\omega^2 H_0^{(2)}(na)}{\alpha_2^2}, \\ a_{31} &= 2ik\mu_1 lJ_1(la), \\ a_{32} &= \rho_1(2k^2\beta_1^2 - \omega^2)J_1(ma), \\ a_{33} &= 0, \\ S_1 &= -V_0 lH_1^{(2)}(la) + ikS_0 H_1^{(2)}(ma), \\ S_2 &= -V_0 \rho_1(2k^2\beta_1^2 - \omega^2)H_0^{(2)}(la) - 2V_0 \rho_1 \beta_1^2 lH_1^{(2)}(la)/a \\ &\quad - 2ik\mu_1 S_0 [mH_0^{(2)}(ma) - H_1^{(2)}(ma)/a], \\ S_3 &= -V_0 \mu_1 2iklH_1^{(2)}(la) - S_0 \rho_1(2k^2\beta_1^2 - \omega^2)H_1^{(2)}(ma). \end{aligned}$$

B. Dispersion relation

The normal-mode dispersion relation, which gives the phase velocity dependence on frequency, is obtained by setting the determinant of Q equal to zero (Ewing *et al.*, 1957). The determinant, Δ , is given by:

$$\Delta = a_{31}(a_{12}a_{23} - a_{13}a_{22}) - a_{32}(a_{11}a_{23} - a_{13}a_{21}). \quad (10)$$

Using the matrix elements given in Eq. (9), the determinant can be expressed as:

$$\begin{aligned} \Delta &= -H_1^{(2)}(na)4k^2\rho_1^2\beta_1^4 lJ_1(la)n \left[mJ_0(ma) - \frac{J_1(ma)}{a} \right] \\ &\quad - H_1^{(2)}(na)\rho_1^2(2k^2\beta_1^2 - \omega^2)J_1(ma)n[(2k^2\beta_1^2 - \omega^2)J_0(la) \\ &\quad + 2\beta_1^2 lJ_1(la)/a] + H_0^{(2)}(na)\rho_1\rho_2\omega^4 lJ_1(la)J_1(ma). \end{aligned} \quad (11)$$

When the radius of the cylinder becomes large, this dispersion relation approaches that of the Scholte wave dispersion relation (Chamuel, 1991), as shown in Appendix A.

When the argument of the Hankel function is large, the phase difference between $H_0^{(2)}$ and $H_1^{(2)}$ is $\pi/2$. As a result, the general case of the dispersion relation, $\Delta=0$, has no solution for real k , meaning that k must be a complex number. This implies that the normal-mode amplitude decreases as z increases, and provides a mathematical description of how the amplitude decays as energy is lost through the cylindrical sample walls and into the confining fluid.

The algebraic solution of Eq. 11 is complicated. To derive a more tractable relation for the GHASTLI experi-

ment, it is assumed that the surrounding medium is not silicone oil, but air, which is a case investigated by Lee and Waite (2009). In Sec. V C, we demonstrate that even with this approximation, the normal-mode predictions are in good agreement with measured results. Additionally, Appendix B demonstrates that a particular feature called the non-dispersive normal mode (NDNM) has no dependence on the surrounding medium's density, so assuming that the surrounding medium is air which yields the same velocity and amplitude predictions that are obtained in the general case of a dense confining fluid.

Given the assumption that air is the confining fluid, applying the boundary conditions of vanishing radial and tangential stresses at $r=a$ yields a determinant given by: $\Delta = a_{21}a_{32} - a_{22}a_{31}$, which is:

$$\begin{aligned} \Delta &= 4k^2\rho_1^2\beta_1^4 lJ_1(la)[mJ_0(ma) - J_1(ma)/a] \\ &\quad + \rho_1^2(2k^2\beta_1^2 - \omega^2)J_1(ma)[(2k^2\beta_1^2 - \omega^2)J_0(la) \\ &\quad + 2\beta_1^2 lJ_1(la)/a]. \end{aligned} \quad (12)$$

As opposed to Eq. (11), there exists a real value of k for the solution of the dispersion relation when l is a real number. Consequently, the normal-mode amplitudes do not vary with respect to distance traveled when acoustic energy is not permitted to leak through the cylindrical boundary. A second consequence of Eq. (12) is the prediction of two distinct types of P-wave normal mode: a nondispersive and a dispersive P-wave normal mode.

The NDNM is a special case in which the phase velocity approaches the P-wave velocity. This forces l toward zero, so Eq. (12) can be approximated by:

$$\Delta \approx \rho_1^2(2k^2\beta_1^2 - \omega^2)^2 J_1(ma). \quad (13)$$

The NDNM solution has a phase velocity, C_0 , satisfying $\Delta=0$ via:

$$(\omega^2 - 2k^2\beta_1^2) = 0, \quad \text{implying } C_0 = \frac{\omega}{k} = \sqrt{2}\beta_1, \quad (14)$$

where β_1 is the shear-wave speed in the cylinder. Equation (14) is identical to the equation derived by Onoe *et al.* (1962).

The dispersive P-wave normal modes (DPNM) also have phase velocities, C , satisfying $\Delta=0$; however, the DPNM solutions are for the more general case in which C does not approach the P-wave speed, l is not vanishingly small, and the full Eq. (12) must be used. There is no simple relation for C in this case, but the dispersion relation can be numerically calculated. Setting $\Delta=0$ in Eq. (12) yields:

$$\frac{\left(1 - \frac{2\beta_1^2}{c_\alpha^2}\right)}{\frac{4\beta_1^3}{c_\alpha^2\alpha_1}} = \frac{l^* J_1(la) \left[m^* J_0(ma) - \frac{\beta_1 J_1(ma)}{a\omega} \right]}{J_1(ma) \left[\left(\frac{2\beta_1^2}{c_\alpha^2} - 1 \right) J_0(la) + \frac{2\beta_1^2 l^* J_1(la)}{a\alpha_1\omega} \right]}, \quad (15)$$

where $l^* = \sqrt{1 - \alpha_1^2/C_\alpha^2}$ and $m^* = \sqrt{1 - \beta_1^2/C_\alpha^2}$. Allowable phase velocities are those for which the left and right sides

FIG. 3. (Color online) Numerical derivation of the theoretical phase velocity when the surrounding medium is air; using parameters for the post-D/R 43% GHBS. Allowable phase velocities are those for which the left side (solid curve) and right side of Eq. (15) (shown at two different frequencies with the dotted and dashed curves) are equal. As the dotted and dashed curves indicate, slight frequency changes significantly alter the location of the intersections of the curves.

of Eq. (15) are equal. These values can be determined graphically as indicated in Fig. 3. As shown in Lee and Waite (2009) and illustrated in Fig. 3, the phase velocities given by Eq. (15) vary rapidly with frequency, complicating the group velocity and amplitude calculations. Depending on the frequency range of interest, however, $J_0(la)$ or $J_1(la)$ may dominate and the other can be set to zero. As shown by Lee and Waite (2009), setting either one of Bessel functions to zero yields a continuous dependence of phase velocity on frequency. As shown in Sec. IV A, this greatly facilitates the differentiation required to obtain an expression for the group velocity.

C. Amplitude

With both a P-wave source and an S-wave source at the origin, the unknown constants A, B, and C in Eq. 9 are given by:

$$\begin{bmatrix} A \\ B \\ C \end{bmatrix} = \frac{1}{\Delta} \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{bmatrix}^T \begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix}, \quad (16)$$

where the matrix element c_{ij} is the cofactor of matrix Q and, Δ is given in Eq. (11). To simplify the mathematics, the same free surface boundary condition used in the dispersion relation derivation is applied. The unknown constants A and B can be derived using A from Eq. (12):

$$A = (S_2 a_{32} - S_3 a_{22}) / \Delta \equiv \frac{A_P(k)}{\Delta(k)}, \quad (17)$$

$$B = (-S_2 a_{31} + S_3 a_{21}) / \Delta \equiv \frac{A_S(k)}{\Delta(k)}.$$

In the following amplitude analysis, only the P-wave is considered. Then,

$$\begin{aligned} A_P(k) = & -V_0 \rho_1^2 (2k^2 \beta_1^2 - \omega^2) J_1(ma) H_0^{(2)}(la) \\ & - V_0 2 \rho_1^2 \beta_1^2 (2k^2 \beta_1^2 - \omega^2) l J_1(ma) H_1^{(2)}(la) / a \\ & - V_0 4k^2 \rho_1^2 \beta_1^4 l H_1^{(2)}(la) [m J_0(ma) - J_1(ma) / a] \\ & - 2i S_0 \rho_1^2 \beta_1^2 k (2k^2 \beta_1^2 - \omega^2) J_1(ma) [m H_0^{(2)}(ma) \\ & - H_1^{(2)}(ma) / a] \\ & + 2i S_0 \rho_1^2 \beta_1^2 k (2k^2 \beta_1^2 - \omega^2) H_1^{(2)}(ma) [m J_0(ma) \\ & - J_1(ma) / a]. \end{aligned} \quad (18)$$

Substituting A into the integral equation shown in Eq. (2), the potential for the P-wave solution is given by the following equation (e.g., Pekeris, 1948; Ewing *et al.*, 1957; Bath, 1968) in the lower half of the complex k -plane:

$$\begin{aligned} \Phi_1(k) = & \int_{-\infty}^{\infty} A(k) J_0(lr) e^{-ikz} dk + V_0 \int_{-\infty}^{\infty} H_0^{(2)}(lr) e^{-ikz} dk \\ = & \int_{\text{Branch cut}} [A(k) J_0(lr) + V_0 H_1^{(2)}(lr)] e^{-ikz} dk \\ & - 2\pi i R^{P_1} - 2\pi i \sum R_n^{P_2} \\ = & \Phi_B + \Phi_{\text{NDNM}} + \Phi_{\text{DPNM}}, \end{aligned} \quad (19)$$

where *Branch cut* is a branch cut integration around the branch points $k_{\alpha_1} = \omega / \alpha_1$ and $k_{\beta_1} = \omega / \beta_1$; R^{P_1} is the residue of integration for the NDNM; $R_n^{P_2}$ is the residue of integration for the DPNM; Φ_B , Φ_{NDNM} , Φ_{DPNM} are the P-wave potentials for the body wave, nondispersive normal mode, and DPNM, respectively. Amplitudes associated with dispersive P- and S-wave normal modes and body waves are discussed in Lee and Waite (2009, 2010). Therefore, only the NDNM amplitude is discussed here.

As discussed in Sec. III B, the existence of NDNM is derived assuming l approaches zero as the phase velocity approaches the P-wave velocity. Taking the dominant term in Eq. (19) as l approaches zero, the constant A becomes

$$\begin{aligned} A = \frac{A_P(k)}{\Delta} \approx & \frac{-2i S_0 \beta_1^2 k m H_0^{(2)}(ma)}{(2k^2 \beta_1^2 - \omega^2)} \\ & + \frac{2i S_0 k \beta_1^2 H_1^{(2)}(ma) m J_0(ma)}{(2k^2 \beta_1^2 - \omega^2) J_1(ma)}. \end{aligned} \quad (20)$$

Equation (20) which depends on the S-wave source strength, S_0 , but not the P-wave source, indicates that the NDNM is generated from the S-wave source and cannot be generated by the P-wave source. This suggests that a critical angle mode conversion from an S-wave to a P-wave at the cylindrical boundary is probably responsible for the NDNM.

FIG. 4. (Color online) Waveform and amplitude spectra of normal modes for post-D/R cycle of GHBS. (A). Normal mode waveforms with cosine tapers applied. Stars indicate the P-wave first arrivals in these shear-transducer waveforms. (B) Amplitude spectra of the waveforms shown in A. Both waveforms have a single dominant peak frequency.

There is a first-order pole in Eq. (17) that corresponds to the phase velocity of the NDNM. The NDNM amplitude can be calculated using Eqs. (19) and (20). Using the residue theorem, the P wave amplitude potential is

$$\Phi_{\text{NDNM}} = -\pi S_0 m J_0(lr) e^{-ikz} \left[H_0^{(2)}(ma) - \frac{H_1^{(2)}(ma) J_0(ma)}{J_1(ma)} \right] \bigg|_{k=\omega/(\sqrt{2}\beta_1)}. \quad (21)$$

The NDNM also exists when the surrounding medium is a fluid other than air. Appendix B derives the dispersion and amplitude relations for NDNM in the case that the surrounding medium is fluid. These NDNM relations with fluid surrounding the sample are the same as that with air surrounding the sample, indicating the surrounding fluid has no effect on the group velocity or amplitude of NDNM.

IV. REAL DATA ANALYSIS

The primary objective for most wave velocity experiments is obtaining the P- and S-wave velocities. As shown in Fig. 2, the P-wave can generally be identified as the onset of the signal, but the S-wave does not always stand out from other large-amplitude features arriving after the P-wave. The theory derived in Sec. III provides a method for identifying these large-amplitude features and through this identification process reveal the S-wave itself.

As demonstrated in Sec. IV B, if the sample contains a NDNM, the S-wave velocity can be calculated directly from the velocity of the more easily identified NDNM. If only DPNM are present between the P- and S-wave arrivals, identifying all the large-amplitude features will likely reveal the S-wave as the feature that does not fit the predicted normal-mode characteristics.

This theory broadens our analytical capacity by providing a method for handling imperfect waveforms in which the

S-wave is not immediately discernable among other large-amplitude features. It is still possible, however, for a waveform to contain too much overlap between features to distinguish between their arrival times, isolate their frequency content, and properly identify each feature (Lee and Waite, 2009).

A. Interpretation of measured velocities in GHBS

Identifying a waveform feature as a particular normal mode requires knowing both the group velocity and dominant frequency of the feature. As discussed in Sec. II A, the waveform feature's velocity can be calculated from the arrival time. Figure 4(A) provides an expanded view of the first arrivals for the post-D/R cycles of 20% and 43% GHBS waveforms shown in Fig. 2. Solid stars in Fig. 4(A) indicate the first P-wave arrivals for each waveform.

The dominant frequency can be obtained from a spectral analysis of a given feature, as shown in Fig. 4(B) for the normal modes indicated in Fig. 4(A). Although the dominant input frequency is 1 MHz, attenuation of the high frequency signal results in much lower dominant frequencies for the observed normal modes. The dominant frequency of the post-D/R 20% GHBS normal mode is about 0.33 MHz, whereas it is about 0.28 MHz for the post-D/R 43% GHBS.

As shown in Lee and Waite (2009), the phase velocity calculated using Eq. (15) varies rapidly depending on frequency and the elastic parameters of the solid, complicating the derivative required in the calculation of group velocity, G :

$$G = \frac{d\omega}{dk} = C + k \frac{dC}{dk}. \quad (22)$$

To approximate a smooth group velocity, an approximate phase velocity is derived from the relation $J_1(la) = 0$, which yields:

FIG. 5. (Color online) Theoretical and measured group velocities for GHBS (solid stars) and for IBS (open stars). The curves are group velocities calculated from Eq. (22) for the $n=0$ to $n=5$ normal modes. The encircled stars are thought to be the nondispersive normal mode (NDNM), rather than the second- ($n=2$) or third-order ($n=3$) normal modes.

$$G_\alpha = \alpha_1 \sqrt{1 - \frac{\alpha_1^2 \Lambda_\alpha^2}{\omega^2 \alpha^2}} = \alpha_1 \sqrt{1 - \frac{\Lambda_\alpha^2}{\Pi_\alpha^2}}, \quad (23)$$

with $\Lambda_\alpha = (5\pi/4 + n\pi)$, $\Pi_\alpha = a\omega/\alpha$, and n is the order of DPNM. Note that in this paper, the order of DPNM is defined from the approximate solution, Eq. (23), not from the more general Eq. (15).

Figure 5 shows approximate group velocities for various orders of DPNM calculated using Eq. (22) with the approximate phase velocity from Eq. (23). Some of the measured

group velocities agree well with the calculated group velocities of various order of n . However, the measured group velocities inside the ellipse, denoted as NDNM, scatter between group velocities calculated with $n=2$ and $n=3$ and these group velocities are independent of the dominant frequency or dimensionless parameter Π_α . As shown later for IBS, these group velocities are close to the velocities predicted for NDNM in Eq. (14). Though Eq. (14) expresses a phase velocity, the phase velocity for NDNM is nondispersive, meaning it is independent of frequency and wave number and therefore equivalent to the NDNM group velocity according to Eq. 22.

B. Interpretation of measured velocities in IBS

For IBS samples described in Sec. II B, the fluid surrounding the sample is air, thus the theory developed here is more accurate than for GHBS surrounded by the more dense silicone oil. Figure 6(A) shows waveforms for IBS with 18%, 34%, and 68% of the pore space saturated with ice. Also shown is the waveform for the 34% IBS after a destabilizing D/R cycle in which the sample is allowed to partially melt before refreezing [Fig. 6(A)]. Like the GHBS, the velocities of the post-D/R 34% IBS are a little higher than those prior to the D/R cycle and the amplitudes for the post-D/R waveforms are much higher than those measured before the D/R cycle. However, as seen in Fig. 6(A), the pre-D/R cycle waveforms clearly show large-amplitude features following the first arrivals, similar to those of GHBS. Figure 6(B) shows the power spectra of the normal modes for the waveforms shown in Fig. 6(A).

Table I presents the measured velocities for IBS and dominant frequencies of the normal-mode propagation. Velocity ratios, the ratio of normal-mode velocity to P-wave velocity, are plotted in Fig. 5 as open stars. The normalized group velocity, G/α_1 , for the IBS is almost constant at 0.86, irrespective of the dominant frequency (see Table I).

When the surrounding fluid is air, Eq. (14) predicts a NDNM with a velocity given by $\sqrt{2}\beta_1$. Table I indicates that the group velocities for IBS are given by 1.43, 1.41, 1.41,

FIG. 6. (Color online) Measured waveforms and power spectra for ice-bearing Ottawa sands (IBS). (A) Waveforms measured using a shear-wave transducer. Solid circles indicate the first P-wave arrival, followed by the normal-mode arrival (stars) and the shear-wave arrival (triangles). The dotted curve for the 34% IBS is the waveform measured after the sample equilibrated following the brief destabilization. (B) Power spectra for waveforms shown in Fig. 6(A), showing the brief destabilization of the 34% IBS (thick dashed curve) causes a measurable increase in the dominant frequency.

FIG. 7. (Color online) (A) Frequency dependence of the radial displacements predicted at $r=0.6$ cm for the nondispersive normal mode using parameters for the 20% IBS (dotted curve) and also with an S-wave velocity reduced by 1% (solid curve). The shaded region shows an uncertainty for the estimation of the dominant frequency from Fig. 6(B). (B) Calculated relative radial displacement of the normal modes shown in Fig. 6(A), summed within the frequency range of the dominant peak frequency (Fig. 6B), with respect to the P-wave velocity.

1.40 times the shear velocity, β_1 , for 18% IBS, 34% IBS, 65% IBS and post-D/R 34% IBS, respectively. These values are within about 1% of the theoretical prediction for NDNM of $\sqrt{2}\beta_1$.

C. Amplitude of the nondispersive normal mode

To make an order-of-magnitude comparison between the measured and the predicted waveform amplitudes, frequency-domain amplitudes are computed. For the NDNM, these amplitudes can be calculated from Eq. (21). Figure 7 shows the relative radial amplitude measured at the shear transducer radius, $r=0.6$ cm, for the post-D/R 34% IBS shown in Table I. As shown in Fig. 7(A), the calculated radial displacement varies significantly with frequency due to numerous constructive and destructive interferences resulting from the multiple internal reflections occurring as acoustic energy traverses the sample.

The NDNM amplitude is also highly sensitive to the elastic velocities in the solid. The dotted curve in Fig. 7(A) was generated using the S-wave velocity increased by about 2% (from 2215 to 2250 m/s) for the post-D/R 34% IBS. Constructive and destructive interference occurs at different frequencies, and the amplitude at the dominant frequency (shaded region) changes significantly due to the small 2% change in S-wave velocity [Fig. 7(A)]. This numerical modeling suggests that substantial waveform differences should be expected from a D/R cycle, given the elastic property changes resulting from briefly destabilizing the sample (Waite *et al.*, 2008).

Comparing NDNM amplitudes based on their dominant frequency ranges is not optimum, because the amplitudes vary significantly with small changes of the dominant frequency. A more stable comparison can be made using the amplitude obtained by integrating the amplitude responses within the observed frequency range. Figure 7(B) shows the

amplitude given by summing the amplitude responses of NDNM calculated over the measured frequency ranges for four IBS samples shown in Table I. The frequency ranges used were 0.13–0.48 MHz, 0.1–0.53 MHz, 0.17–0.70 MHz, and 0.17–0.62 MHz for the pre-D/R 18% IBS, 34% IBS, and 65% IBS and post-D/R 34% IBS, respectively. The summed-amplitude responses shown in Fig. 7(B) are proportional to the corresponding time-domain normal-mode amplitudes shown in Fig. 6(A). In both Figs. 6(A) and 7(B), the pre-D/R 34% IBS has the smallest amplitude, followed by pre-D/R 18% IBS, and post-D/R 34% IBS. The agreement does not hold for the 65% pre-D/R IBS case, but if the S-wave velocity is changed from 2510 to 2490 m/s; the calculated amplitude, denoted as an open star in Fig. 7(B), and the measured amplitude in Fig. 6(A) are indeed the largest of the normal-mode amplitudes. This again emphasizes that the waveguide characteristics of IBS are highly sensitive to the elastic properties of IBS.

V. DISCUSSION

A. Wave guide characteristics of GHBS

As illustrated in Fig. 2, a D/R cycle causes obvious changes in normal-mode amplitudes and velocities, but has a smaller impact on the measured P- and S-wave velocities. This discrepancy provides an insight into the normal-mode propagation and wave-guide character of cylindrical GHBS and IBS samples.

As shown by X-ray CT imagery (Waite *et al.*, 2008), GHBS subjected to a brief destabilization will initially experience hydrate dissociation near the sample surface. As the sample is restabilized, water from that dissociated hydrate migrates toward the sample's central axis and reforms as hydrate. The density decrease as a function of radius in the GHBS becomes more pronounced, as a result changing the wave-guide characteristics of the sample by changing the

nature of the internal reflections governing how the normal-modes propagate.

P- and S- waves, in contrast, traverse the direct line between the transducers along the sample axis. This is the least-disturbed region of the sample, and the observed P- and S-wave speeds are, indeed, less affected by the D/R cycle than are the normal modes in GHBS. In contrast, Fig. 6(A) and Table I indicate a brief destabilization changes of the P-wave, S-wave, and normal-mode velocities on similar scales in IBS. This suggests that IBS may form higher ice saturations near the sample surface during the initial freeze, which cools faster than the sample interior, and the P- and S-waves travel along the outer part of the sample to a much greater degree than in GHBS. The precise impact of ice formation and a subsequent destabilization cycle on the density profile of IBS is still under investigation.

B. Nondispersive normal-mode amplitude

Whereas P- and S-wave sources can excite the DPNM (Lee and Waite, 2009), the normal-mode theory predicts that only an S-wave source can generate a nondispersive normal mode (NDNM). Given the S-wave crystal's inefficiency in producing P-waves, the large NDNM amplitude suggests it is generated as a shear wave. The energy is then converted to a P-wave during a reflection from the cylindrical boundary. In this instance, the theoretical amplitude derivation provides specific information about the behavior of acoustic waves in the cylindrical sample. In general, however, the amplitude relations should only be relied upon for order-of-magnitude amplitude comparisons between features. Two issues limit the quantitative use of the amplitude relations: (1) assuming the wavenumber, k , is real and (2) assuming the transducers are ideal omni-directional sources.

The assumption that k is the real cause for spectral holes in the amplitude spectrum. For example, the NDNM amplitudes have spectral holes when $J_1(ma) = 0$, or $\omega = \sqrt{2}\beta_1\pi(5/4 + n)/a$. This means the frequency interval of the spectral hole, f_h , is $f_h = \sqrt{2}\beta_1/(2a)$, or ~ 0.45 MHz for the post-D/R 34% IBS. As expected, the amplitude peaks shown in Fig. 7(A) are separated by 0.45 MHz. To avoid these high-amplitude predictions resulting from spectral holes, k should be a complex number.

The second assumption limiting the quantitative effectiveness of the amplitude relations is that the theoretical sources are ideal and uniformly omni-directional. In reality, the experimental transducers have certain radiation patterns, meaning the P-wave source is stronger than the S-wave source in certain directions and weaker in others. Without incorporating the true source radiation pattern into the theory, the calculated amplitude will not agree with the measured amplitude exactly. As discussed above, however, relative magnitudes of the normal-mode and body-wave features can be assessed.

C. Effect of the surrounding medium

1. Velocity

As discussed in Sec. III B, the existence of NDNM is derived from Eq. (12) for the case with no confining fluid by assuming that the NDNM phase velocity approaches the

P-wave velocity, forcing l to zero. When dense confining fluid surrounds the sample, the phase velocity is calculated from Eq. (11). Making the same assumption about the NDNM phase velocity approaching the P-wave velocity again forces l to zero, and the normal-mode phase velocity again becomes $C_0 = \sqrt{2}\beta_1$. Therefore, the NDNM can exist regardless of the confining fluid density.

NDNM are observed in all IBS samples but not in all GHBS samples, suggesting a difference in their internal structures. In 20% GHBS, the pre-D/R signal falls in the expected range for NDNM based on the expected shear-wave speed (Fig. 5). After the D/R cycle, however, the observed normal mode has a velocity and frequency that match well with the predicted second-order DPNM (Fig. 5) and exceeds the expected phase velocity of an NDNM given the measured shear-wave speed. These predictions are calculated using the no-confining fluid simplification, suggesting that the confining fluid surrounding the 20% GHBS does not significantly impact the normal-mode velocities. The velocities seem much more sensitive to the sample's internal structure instead. In the 20% GHBS case, the D/R cycle appears to have obscured the NDNM, but augmented the second-order DPNM.

The 43% GHBS results also illustrate the sensitivity of the normal mode to the sample's internal structure, as well as pointing out variability due to the transducer crystal and coupling between the transducer and sample. Figure 8 compares waveforms measured on the post-D/R cycle 43%

FIG. 8. (Color online) Waveforms measured for the 43% GHBS measured in 2006 (dotted curve) and 2007 (solid curve). The P-wave arrival (solid circle) is quite distinct from the normal-mode arrival (star) in the 2006 case, but much less so in the 2007 measurement of a different 43% GHBS sample. The type of normal mode seems to have changed as well. These differences are partly due to a difference in the transducers used and partly due to differences in the internal structure of the sample.

GHBS samples in 2006 and then again in 2007 on a different sample, using a different endcap set with new transducer crystals. The compressional body wave arrivals differ, indicating a difference in elastic properties between the samples. The delay between the P-body wave and the subsequent normal-mode arrival is a more significant difference between the waveforms, however. In the 2006 case, the normal-mode velocity is only 4% higher than that predicted by $C_0 = \sqrt{2}\beta_1$, suggesting the mode is an NDNM. In 2007, the normal-mode velocity is 10% higher than that predicted for the NDNM with the velocity better fitting the prediction for a second-order DPNM (Fig. 5). The second-order DPNM is fast enough to overlap the P-body wave, meaning that the large-amplitude feature observed in the 2007 waveform resulted from a mixture of the body wave and normal-mode energies.

Waveform differences observed between the 2006 and 2007 43% post-D/R cycle GHBS samples are due to slight differences in elastic properties, or differences in the transducers. Regardless of the cause, however, differences observed between the 43% GHBS samples and the pre- and post-D/R cycle differences observed in the 20% GHBS sample indicate the first large-amplitude arrival following the compressional body wave cannot be assumed to be a particular mode without first establishing its dominant frequency and velocity relative to the predictions for both dispersive and nondispersive normal modes.

2. Amplitude

The algebraic solution for the NDNM amplitude for cylinders surrounded by dense confining fluid is given in Appendix B. As shown in the appendix, the amplitudes are identical to the case where air is the confining fluid [Eq. (21)]. For the NDNM, at least, velocity and amplitude are independent of the type of confining fluid.

The algebraic solution for DPNM amplitudes is complicated in the case of a dense confining fluid, such as silicone oil. As a result, the confining fluid is ignored in our amplitude derivation for the DPNM and only relative amplitudes are used to characterize the measured waveforms. Magnitudes of the DPNM amplitudes in samples surrounded by dense confining fluid are not known at this time. As shown in Lee and Waite (2009), however, the DPNM amplitudes include a complex value of the wavenumber, k , and are predicted to decay with sample length, as with the P- and S-body wave amplitudes (Lee and Waite, 2009).

VI. CONCLUSION

Acoustic waveforms measured through cylindrical samples that are long relative to the acoustic wavelength contain large-amplitude features than can obscure the P- or S-body waves. These features can be characterized as normal modes, created by the constructive interference of acoustic energy that has undergone internal reflections off the cylindrical sample walls while traversing the sample. The normal-mode propagation theory presented here provides a tool for identifying these high-amplitude features given their frequency content and group velocity.

As a check on the normal-mode theory, the theoretical amplitudes of the normal modes were derived and found to be in qualitative agreement with the observed amplitudes. This agreement includes capturing the low nondispersive normal-mode amplitude for the 34% IBS sample relative to the 18% and 65% IBS samples.

Based on the results of the investigation presented here, three primary conclusions can be drawn regarding waveforms measured on cylindrical samples that are long compared with the acoustic wavelength:

- (1) Shear-wave transducers can generate a NDNM that travels with a velocity $C_{\text{NDNM}} = \sqrt{2}\beta_1$, where β_1 is the shear-wave speed through the sample. When the NDNM is visible, as it was visible in both GHBS and IBS; it can be used to estimate the sample's shear-wave speed.
- (2) Because normal modes require reflections of acoustic energy off the cylindrical sample walls, they are sensitive to changes in the sample's internal structure. As demonstrated in the GHBS, a redistribution of gas hydrate in the sample can suppress the NDNM, essentially replacing it with a second-order DPNM that cannot be easily used to deduce the sample's shear-wave speed. Normal modes cannot be identified simply from their approximate location in the waveform; they must be characterized based on their dominant frequency and group velocity.
- (3) The normal-mode sensitivity to internal reflections off the sample surface implies a dependence on the properties of the confining fluid in contact with that sample surface. This dependence complicates the normal-mode analysis, but a simplification based on assuming the confining fluid density is zero yields dispersive normal-mode velocity estimates that are in good agreement with measured results for GHBS. For NDNM, the predicted velocity is shown mathematically to be independent of the confining fluid density.

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APPENDIX A: DISPERSION RELATION OF A SCHOLTE WAVE

The dispersion relation for a solid surrounded by fluid is given by:

$$\Delta = -H_1^{(2)}(na)4k^2\rho_1^2\beta_1^4J_1(la)n\left[mJ_0(ma) - \frac{J_1(ma)}{a}\right] - H_1^{(2)}(na)\rho_1^2(2k^2\beta_1^2 - \omega^2)J_1(ma)n[(2k^2\beta_1^2 - \omega^2)J_0(la) + 2\beta_1^2J_1(la)/a] + H_0^{(2)}(na)\rho_1\rho_2\omega^4J_1(la)J_1(ma). \quad (A1)$$

When the cylinder radius becomes large, the dispersion relation becomes:

$$\begin{aligned}\Delta = & -H_1^{(2)}(na)4k^2\rho_1^4\beta_1^4J_1(la)nmJ_0(ma) \\ & - H_1^{(2)}(na)\rho_1^2(2k^2\beta_1^2 - \omega^2)J_1(ma)n(2k^2\beta_1^2 - \omega^2)J_0(la) \\ & + H_0^{(2)}(na)\rho_1\rho_2\omega^4lJ_1(la)J_1(ma).\end{aligned}\quad (\text{A2})$$

If the phase velocity is less than the body wave velocities, the wave numbers l , m , and n become purely imaginary numbers. At high frequencies, setting the determinant Eq. (A2) to zero yields,

$$\begin{aligned}-4k^2\rho_1\beta_1^4lm - \rho_1(2k^2\beta_1^2 - \omega^2)(2k^2\beta_1^2 - \omega^2) \\ + \rho_2\omega^4l/n = 0.\end{aligned}\quad (\text{A3})$$

Rearranging Eq. (A3),

$$\begin{aligned}4k^2\beta_1^4\sqrt{k^2 - \frac{\omega^2}{\alpha_1^2}}\sqrt{k^2 - \frac{\omega^2}{\beta_1^2}} - k^4\beta_1^4\left(2 - \frac{\omega^2}{k^2\beta_1^2}\right)^2 \\ = \frac{\rho_2\omega^4\sqrt{k^2 - \omega^2/\alpha_1^2}}{\rho_1\sqrt{k^2 - \omega^2/\alpha_2^2}}.\end{aligned}\quad (\text{A4})$$

In terms of the wave velocity $c = \omega/k$, Eq. (A4) can be written,

$$4\sqrt{1 - \frac{c^2}{\alpha_1^2}}\sqrt{1 - \frac{c^2}{\beta_1^2}} - \left(2 - \frac{c^2}{\beta_1^2}\right)^2 = \frac{\rho_2c^4\sqrt{1 - c^2/\alpha_1^2}}{\rho_1\beta_1^4\sqrt{1 - c^2/\alpha_2^2}}.\quad (\text{A5})$$

If $\beta_1 > c > \alpha_2$ and a becomes large, $H_1^{(2)}(na) = iH_0^{(2)}(na)$ in Eq. (A2), meaning Eq. (A5) becomes,

$$4\sqrt{1 - \frac{c^2}{\alpha_1^2}}\sqrt{1 - \frac{c^2}{\beta_1^2}} - \left(2 - \frac{c^2}{\beta_1^2}\right)^2 = \frac{i\rho_2c^4\sqrt{1 - c^2/\alpha_1^2}}{\rho_1\beta_1^4\sqrt{c^2/\alpha_2^2 - 1}},\quad (\text{A6})$$

which is the dispersion relation for the Scholte wave (Chamuel, 1991).

When ρ_2 becomes 0 and a becomes large, as in the case of a free surface or air over a solid half-space, Eqs. (A5) and (A6) become,

$$4\sqrt{1 - \frac{c^2}{\alpha_1^2}}\sqrt{1 - \frac{c^2}{\beta_1^2}} - \left(2 - \frac{c^2}{\beta_1^2}\right)^2 = 0,\quad (\text{A7})$$

which is identical to the Rayleigh wave dispersion relation (White, 1965).

APPENDIX B: NONDISPERSIVE NORMAL MODE WHEN FLUID SURROUNDS THE SAMPLE

The dispersion relation shown in Eq. (11) can be reduced to the following equation, as l becomes small,

$$\Delta = \rho_1^2(2k^2\beta_1^2 - \omega^2)^2J_1(ma)nH_1^{(2)}(na).\quad (\text{B1})$$

The requirement $\Delta = 0$ yields the same dispersion relation shown in Eq. (13), meaning that NDNM exists when the surrounding medium is fluid.

The constant A for P-wave and S-wave sources can be written as,

$$\begin{aligned}A_p(k)\Delta = & -a_{23}a_{32}S_1 + a_{13}a_{32}S_2 + (a_{12}a_{23} - a_{13}a_{22})S_3 \\ = & V_0\rho_1\rho_2\omega^2l(2k^2\beta_1^2 - \omega^2)H_1^{(2)}(la)J_1(ma)H_0^{(2)}(na) \\ & + V_0\rho_1^2(2k^2\beta_1^2 - \omega^2)^2nH_0^{(2)}(la)J_1(ma)H_1^{(2)}(na) \\ & - V_02\rho_1\rho_2\beta_1^2k^2\omega^2lH_1^{(2)}(la)J_1(ma)H_0^{(2)}(na) \\ & + V_04k^2\rho_1^2\beta_1^4lmnH_1^{(2)}(la)J_0(ma)H_1^{(2)}(na) \\ & - S_0ik\rho_1\rho_2\omega^2(2k^2\beta_1^2 - \omega^2)J_1(ma)H_1^{(2)}(ma) \\ & \times H_0^{(2)}(na) + S_02ik\rho_1^2\beta_1^2(2k^2\beta_1^2 - \omega^2)nmJ_1(ma) \\ & \times H_0^{(2)}(ma)H_1^{(2)}(na) + S_0ik\rho_1\rho_2\omega^2(2k^2\beta_1^2 - \omega^2) \\ & \times J_1(ma)H_1^{(2)}(ma)H_0^{(2)}(na) - S_02ik\rho_1^2\beta_1^2(2k^2\beta_1^2 - \omega^2) \\ & \times nmJ_0(ma)H_1^{(2)}(ma)H_1^{(2)}(na)\end{aligned}\quad (\text{B2})$$

The fifth and seventh term cancel each other in Eq. (B2). Using Eq. (B1) and the same approximation derived for the case of air being the surrounding medium, the constant A contributing to NDNM is given by:

$$A \approx \frac{-2iS_0km\beta_1^2H_0^{(2)}(ma)}{(2k^2\beta_1^2 - \omega^2)} + \frac{2iS_0km\beta_1^2H_1^{(2)}(ma)J_0(ma)}{(2k^2\beta_1^2 - \omega^2)J_1(ma)}.\quad (\text{B3})$$

This is identical to the constant A derived for air being the surrounding medium in Eq. (20) in the main text. Therefore, the type of fluid surrounding the solid does not affect the NDNM velocity or amplitude.

- Aki, K., and Richards P. G. (1980). *Quantitative Seismology – Theory and Methods* (Freeman and Co., New York), 932 pp.
- Archer, D. (2007). “Methane hydrate stability and anthropogenic climate change,” *Biogeosciences* **4**, 521–544.
- ASTM (2004). D 4767-4, Standard test method for consolidated undrained triaxial compression test for cohesive soils, in *Annual Book of ASTM Standards*, edited by ASTM International (American Society for Testing and Materials, West Conshohocken, PA), 13 p.
- ASTM (2005). E 494-05, Standard practice for measuring ultrasonic velocity in materials, in *Annual Book of ASTM Standards*, edited by ASTM International (American Society for Testing and Materials, West Conshohocken, PA), 13 p.
- Ayling, M. R., Meredith, P. G., and Murrell, S. A. F. (1995). “Microcracking during triaxial deformation of porous rocks monitored by changes in rock physical properties, I. Elastic-wave propagation measurements on dry rocks,” *Tectonophysics* **245**, 205–221.
- Bath, M. (1968). *Developments in Solid Earth Geophysics* (Elsevier Publishing Co., New York), 415 pp.
- Biot, M. (1952). “Propagation of elastic waves in a cylindrical bore containing a fluid,” *J. Appl. Phys.* **23**, 997–1009.
- Boswell, R. (2009). “Is gas hydrate energy within reach?,” *Science* **325**, 957–958.
- Chamuel, J. R. (1991). “Laboratory studies on pulsed leaky Rayleigh wave components in a water layer over a solid bottom,” in *Shear waves in Marine Sediment*, edited by J. M. Hovem, et al. (Kluwer Academic Publishers, Dordrecht, Netherlands), pp. 59–66.
- Collett, T. S., Riedel, M., Boswell, R., Cochran, J. R., Kumar, P., Sethi, A. K., Sathe, A. V., and Party, N. E.-S. (2006). “International team completes landmark gas hydrate expedition in the offshore of India,” *Fire in the Ice*:

- Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, Methane Hydrate Newsl. **Fall 2006**, 1–4.
- Ewing, W. M., Jardetzky, W. S., and Press, F. (1957). *Elastic Waves in Layered Media* (McGraw-Hill, New York), 380 pp.
- Expedition 311 Scientists (2006). “Expedition 311 summary,” in *Proceedings Of IODP, 311*, edited by M. Riedel *et al.*, Integrated Ocean Drilling Program Management International, Inc., Washington, DC.
- Graff, K. F. (1975). *Wave Motion in Elastic Solids* (Dover Publications, Inc., New York), 649 pp.
- Grant, F. S., and West, G. F. (1965). *Interpretation Theory in Applied Geophysics* (McGraw-Hill, New York), 583 pp.
- Helgerud, M. B., Waite, W. F., Kirby, S. H., and Nur, A. (2009). “Elastic wave speeds and moduli in polycrystalline ice Ih, sI methane hydrate, and sII methane-ethane hydrate,” *J. Geophys. Res.* **114**, B02212.
- Honarvar, F., Enjilela, E., Sinclair, A. N., and Mirnezami, S. A. (2007). “Wave propagation in transversely isotropic cylinders,” *Int. J. Solids Struct.* **44**, 5236–5246.
- Kolsky, H. (1963). *Stress Waves in Solids* (Dover Publications, Inc., New York), 213 pp.
- Kvenvolden, K. A., and Lorenson, T. D. (2001). “The global occurrence of natural gas hydrates,” in *Natural Gas Hydrates: Occurrence, Distribution and Detection*, edited by C. K. Paull and W. P. Dillon (American Geophysical Union, Washington, DC), Vol. 124, pp. 3–18.
- Lee, M. W. (2002). “Biot-Gassmann theory for velocities of gas hydrate-bearing sediments,” *Geophysics* **67**, 1711–1719.
- Lee, M. W., and Balch, A. H. (1982). “Theoretical seismic wave propagation from a fluid-filled borehole,” *Geophysics* **47**, 1308–1314.
- Lee, M. W., and Waite, W. F. (2009). High Frequency Normal Mode Propagation in Aluminum Cylinders, Scientific Investigation Report 2009–5142 (U.S. Geological Survey, Reston, Virginia), 24 pp.
- Lee, M. W., and Waite, W. F. (2010). Shear-wave Normal Mode Propagation in Aluminum Cylinders, Scientific Investigation Report 2010–5013 (U.S. Geological Survey, Reston, Virginia), 25 pp.
- Leg 204 Shipboard Scientific Party (2003). “Explanatory notes,” in *Proceedings of ODP*, Initial Reports, 204, edited by A. M. Tréhu *et al.*, College Station, TX, pp. 1–102.
- Matsushima, J. (2006). “Seismic wave attenuation in methane hydrate-bearing sediments: Vertical seismic profiling data from the Nankai Trough exploratory well, offshore Tokai, central Japan,” *J. Geophys. Res.* **111**, B10101.
- McIver, R. D. (1982). “Role of naturally occurring gas hydrates in sediment transport,” *AAPG Bull.* **66**, 789–792.
- Mirsky, I. (1965). “Wave propagation in transversely isotropic circular cylinders, Part I: Theory,” *J. Acoust. Soc. Am.* **37**, 1016–1021.
- Onoe, M., McNiven, H. D., and Mindlin, R. D. (1962). Dispersion of axially symmetric waves in elastic rods,” *J. Appl. Mech.* **29**, 729–734.
- Pekeris, C. L. (1948). *Theory of Propagation of Explosive Sound in Shallow Water*, Memoir 27 (Geological Society of America, New York), 117 pp.
- Priest, J. A., Best, A., and Clayton, C. R. (2005). “A laboratory investigation into the seismic velocities of methane gas hydrate-bearing sand,” *J. Geophys. Res.* **110**, B04102.
- Rinehart, J. S. (1975). *Stress Transients in Solids* (HyperDynamics, Sante Fe, NM), 230 pp.
- Santamarina, J. C., Klein, K. A., and Fam, M. A. (2001). *Soils and Waves: Particulate Materials Behavior, Characterization and Process Monitoring* (John Wiley & Sons, Ltd., New York), 488 pp.
- Waite, W. F., Kneafsey, T. J., Winters, W. J., and Mason, D. H. (2008). “Physical property changes in hydrate-bearing sediment due to depressurization and subsequent repressurization,” *J. Geophys. Res.* **113**(B07102), 12.
- Waite, W. F., Winters, W. J., and Mason, D. H. (2004). “Methane hydrate formation in partially water-saturated Ottawa sand,” *Am. Mineral.* **89**, 1202–1207.
- White, J. E. (1965). *Seismic Waves – Radiation, Transmission and Attenuation* (McGraw-Hill, New York), 302 pp.
- Winters, W. J., Dillon, W. P., Pecher, I. A., and Mason, D. H. (2000). “GHASTLI; determining physical properties of sediment containing natural and laboratory-formed gas hydrate,” in *Natural Gas Hydrate in Oceanic and Permafrost Environments*, edited by M. D. Max (Kluwer Academic Publishers, Dordrecht, Netherlands), pp. 311–322.
- Yun, T. S., Francisca, F. M., Santamarina, J. C., and Ruppel, C. (2005). “Compressional and shear wave velocities in uncemented sediment containing gas hydrate,” *Geophys. Res. Lett.* **32**, L10609.
- Zhou, W. J., Ichchou, M. N., and Mencik, J. M. (2009). “Analysis of wave propagation in cylindrical pipes with local inhomogeneities,” *J. Sound Vib.* **319**, 335–354.