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Phonons in porous media at intermediate frequencies

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Using ultrasonic techniques, the phonon diffusion coefficient and density of states have been measured at intermediate frequencies in a porous solid network of sintered glass beads. A transition to a very strong scattering regime is observed, whereupon the diffusion coefficient becomes independent of frequency. Near crossover, the density of states is enhanced and exhibits a broad maximum. These data are in good overall agreement with a lattice-based percolation model, and give additional insight into the effects of strong scattering on phonon transport in disorderd media.

1 Introduction Porous media form an interesting class of mesoscopic materials, whose structure at length scales between atomic dimensions and bulk dramatically influence their phonon properties. Examples include packed powders, porous sintered particle networks, aerogels and foams [1–5]. In the low frequency, long wavelength limit, the medium appears uniform and the phonons propagate ballistically, but with a reduced velocity that reflects the weakening of the structure due to its porosity. By contrast, at intermediate frequencies where the wavelength is comparable with the pore size, the scattering can become very strong and the nature of wave propagation is substantially modified. Thus, wave propagation is expected to become diffusive, and the phonons may even become localized. In materials such as sinters, where the basic building block of the structure is much larger than atomic dimensions, a third high frequency regime exists at wavelengths less than the particle size, where phonons propagate freely inside the particles and their character is similar to uniform bulk materials.

In this paper, we study the intermediate frequency regime, using ultrasonic techniques to investigate the vibrational modes of a model porous material formed from sintered networks of spherical glass particles. We show that very strong scattering is indeed observed, and directly measure the phonon diffusion coefficient over more than a decade in frequency. The transition to the strong scattering regime is marked by the onset of a plateau in the diffusion coefficient, which is found to be remarkably small. To obtain complementary information on the nature of the vibrational modes of these sintered networks, we also investigate the density of states in and above the crossover region using a novel mode counting technique [5]. Insight into these experimental results is provided by numerical simulations of phonon transport in a model 3D lattice percolation system [6, 7], originally performed to elucidate the thermal conductivity plateau in glasses, and by the extensive theoretical work on vibrational localization and transport in random media stimulated by the pioneering ideas of Alexander and Orbach [8].

2 Diffusion of ultrasonic waves in glass bead sinters The samples used in our experiments were prepared by sintering 100-μm-diameter glass beads to form a porous network of fused particles at a volume fraction ϕ_{glass} of 0.30. To achieve this low volume fraction, the glass beads were first mixed in a 1-1

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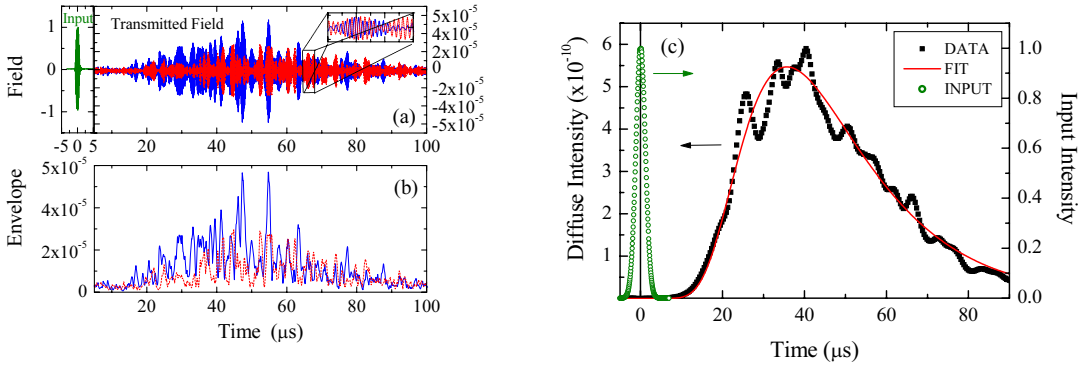

Fig. 1 (color online) (a) Transmitted field through a sintered glass bead network in two different speckle spots compared with the input pulse (left), (b) corresponding field envelopes, and (c) diffuse intensity time-of-flight profile. The frequency is 6.5 MHz, and L/a = 130, where L is the thickness and a is the glass bead radius.

ratio with iron filler particles of the same diameter, and the iron particles were subsequently removed by etching in acid after sintering the glass at 700 °C.

To investigate wave transport through these porous samples, we used a pulsed technique in which the sample was waterproofed and placed in a water tank between an immersion transducer, which generated the input pulse, and a miniature hydrophone detector [9]. The hydrophone was scanned across the surface (3 mm away) to detect the transmitted field in individual speckle spots. Typical examples of the detected field at two different positions are shown in Fig. 1(a). This figure clearly shows that the transmitted waves undergo strong multiple scattering, since the detected field is stretched out in time over many, many input pulse widths as the ultrasonic waves travel longer and longer paths through the sample. To measure the diffusion coefficient, the time profile of the ensemble averaged intensity is determined from the transmitted field profile in each speckle by first finding the envelope of the transmitted fields (Fig. 1(b)), and then ensemble averaging the square of the envelopes over 121 speckles to obtain the average transmitted intensity. An example of the diffusive profile at 6.5 MHz (with a bandwidth of 0.2 MHz) is shown in Fig. 1(c). The diffusion coefficient is determined by comparing the data with the predictions of the diffusion approximation in which the boundary conditions on the sample and the effects of absorption are correctly included [9]. The solid curve in Fig. 1(c) shows such a fit of the diffusion model to our data, demonstrating that excellent fits are obtained and allowing reliable values of the diffusion coefficient to be determined. Fig. 1(c) also shows that a single diffusive pulse is observed, even though the sinter is an elastic material supporting both longitudinal and transverse waves. This occurs since the longitudinal and transverse polarizations mix due to mode conversion at each scattering event, so that after travelling only a few mean free paths the diffuse energy becomes equipartitioned between the two polarizations [10] and the measured diffusion coefficient is determined by an energy-density-weighted average.

The frequency dependence of the diffusion coefficient is shown in Fig. 2(a). At low frequencies, D drops rapidly with frequency, reflecting the rapid decrease in the mean free path as the wavelength becomes comparable with the sizes of the pores in the structure. Above the crossover frequency $f_0 \sim v_p / 2\pi\xi = 0.8$ MHz, where v_p is the phase velocity and $\xi \sim 6a$ is the correlation length at $\phi_{\text{glass}} = 0.3$ [3], the scattering is very strong and D becomes almost independent of frequency. These data are compared in the insert of Fig. 2(a) with a theoretical calculation and numerical simulation of wave transport in a random medium consisting of atoms arranged in a cubic lattice in which only 65% of the lattice sites are occupied [6]. While this calculation was originally performed to help understand the anomalous low-temperature thermal conductivity of glasses, the model corresponds very well to our experiment, as both theoretical and experimental systems are examples of percolating structures well above the percolation threshold. The striking plateau seen in both experiment and theory is attributed to the frequency independence of the transport mean free path in this strong scattering regime, where it reaches its minimum value given by the bead diameter in our experiment or the lattice constant in the theory. Our measurements of D in glass bead sinters are the first to directly confirm this prediction experimentally.

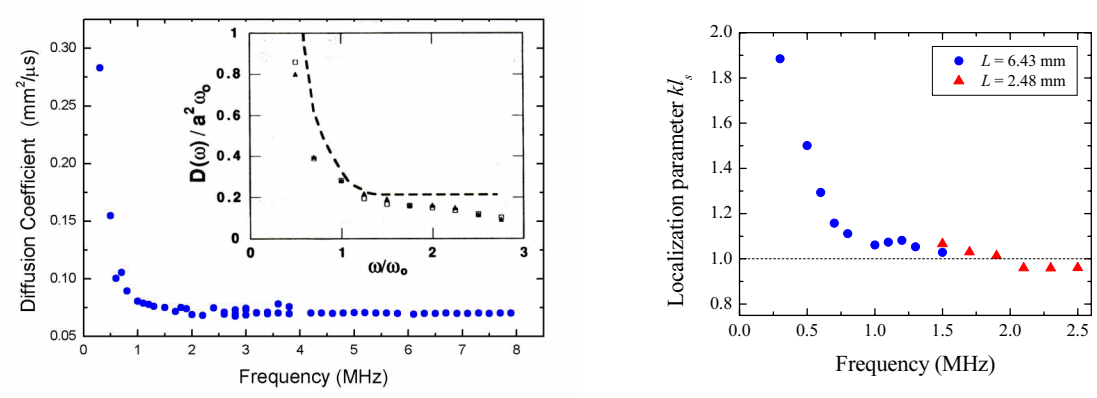

Fig. 2 (colour online) (a) (left) Frequency dependence of the diffusion coefficient. The inset shows predictions of Ref. [6]. (b) (right) Localization parameter as a function of frequency.

In the crossover region, we have also been able to detect the weak ballistic pulse that propagates through the sinter without scattering out of the forward direction [11], and measure the longitudinal scattering mean free path l_s, as well as the phase and group velocities. As a result, we can determine the wave vector k and the localization parameter kl_s, which decreases with frequency and gradually approaches a value close to one near crossover (Fig. 2(b)). This confirms that the scattering is very strong, but the modes do not appear to be localized, as we have also examined the statistics of the intensity fluctuations in the speckle pattern and found them to be Rayleigh-like [12]. Thus the Ioffe-Regel criterion $kl_s < 1$ does not necessarily imply localization for acoustic or elastic waves.

3 Density of states To gain additional insight into the nature of the vibrational modes, we have measured the density of states by directly counting the modes in the frequency domain [5]. This technique requires sufficiently small samples (typically ~ 1 mm^3) that the individual modes can be resolved in the fast Fourier transform of the transmitted wave field that is measured in a pulsed ultrasonic experiment. Both irregular and cube-shaped pieces were cut from a larger sample and carefully placed between two broadband transducers, relying on gentle contact to weakly couple the acoustic energy into and out of the sample. To eliminate any signals travelling through the air, and to reduce losses that increase the width of the modes, the measurements were performed in vacuum. Figure 3(a) shows the modal structure in the crossover region for a small irregularly shaped sample similar to the one in the insert. By binning the peak counts and normalizing with respect to volume, the average density of states for many samples is obtained.

Figure 3(b) shows the frequency dependence of the density of states measured by this mode counting technique near and above the crossover to the intermediate frequency regime. The data exhibit a broad maximum near crossover, with a gradual decrease at higher frequencies. Also shown is the density of states calculated using the Debye approximation from our ballistic measurements of the phase and group velocities. Note the weaker frequency dependence, compared to the usual f^2 Debye model behaviour, due to the measured increase of both the phase and group velocities with frequency in the crossover regime. Interestingly, the complete density of states measured by mode counting is larger than the Debye prediction from the ballistic data. Figure 3(b) compares our results with a simple model [2] that delineates the three regimes outlined in the Introduction: (i) a low frequency effective medium regime with Debye-like modes having low velocities compared with bulk glass, (ii) an intermediate frequency regime where the modal density is assumed for simplicity to be constant, and (iii) a high frequency bulk glass regime, also described by the Debye approximation. The low frequency transition occurs at the crossover frequency f_0, while the high frequency transition occurs when the wavelength of bulk glass modes is twice the diameter of the particles. The value of the constant in the intermediate frequency regime is determined by the condition that total number of modes is fixed by the number of degrees of freedom.

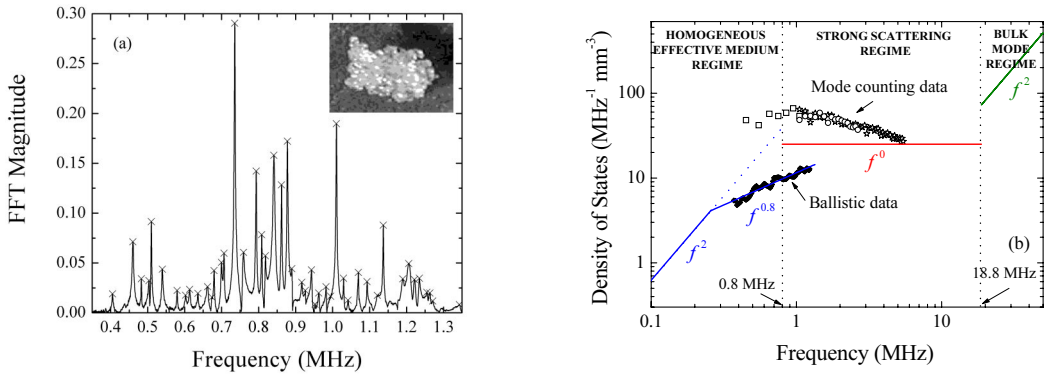

Fig. 3 (a) Modes of a small sinter sample like the one shown in the insert. (b) Density of states measured by mode counting (open symbols) and calculated from the measured ballistic velocities (closed symbols). The solid lines are predictions of a simple model for the three phonon regimes in porous media (see text).

Note that the constant density of states assumed in this model is very close to the predictions of the fracton model for this sintered glass material, where the value of the fracton dimension was found from low frequency velocity measurements to be 1.05 [3], giving a density of states proportional to $f^{0.05}$. It is interesting that the total measured density of states is significantly enhanced relative to this prediction near the lower crossover region, a result that is consistent with more recent simulations of atomic glassy systems [7, 13].

4 Conclusions We have measured the phonon diffusion coefficient and density of states at intermediate frequencies in a porous, strongly scattering solid material made from sintered glass beads. When the scattering becomes so strong that the localization parameter kl_s approaches unity, the diffusion coefficient reaches a plateau, where D is remarkably small. The density of states is enhanced and exhibits a broad maximum near the crossover to this strong scattering regime. There is a striking similarity between these experimental results and recent theoretical predictions and numerical simulations for atomic glasses near the thermal conductivity plateau around 10 K [13]. This suggests that ultrasonic experiments in sinter, which may be viewed as a "mesoscopic glass" in which the beads play the role of atoms, may be of interest investigating directly how the dominant phonon modes are modified by strong scattering in the vicinity of the thermal conductivity plateau, as the frequency dependence of the diffusion coefficient, the density of states and the scattering mean free path can all be measured independently.

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References

[1] R. O. Pohl, in: Amorphous Solids, Vol. 24 of Topics in Current Physics, edited by W. A. Phillips (Springer, New York, 1981), p. 27.
[2] M. C. Maliepaard, J. H. Page, J. P. Harrison, and R. J. Stubbs, Phys. Rev. B **32**, 6261 (1985).
[3] H. P Schriemer, N. G. Pachet, and J.H. Page, Waves in Random Media **6**, 361 (1996).
[4] E. Courtens, R. Vacher, J. Pelous, and T. Woignier, Phys. Rev. Lett. **58**, 128 (1987).
[5] O. I. Lobkis and R. L. Weaver, J. Acoust. Soc. Am. **109**, 2636 (2001).
[6] P. Sheng, M. Zhou, and Z-Q. Zhang, Phys. Rev. Lett. **72**, 234 (1994).
[7] P. Sheng and M. Zhou, Science **253**, 539 (1991).
[8] For a review, see T. Nakayama, K. Yakubo, and R. L. Orbach, Rev. Mod. Phys. **66**, 381 (1994).
[9] J. H. Page, H. P. Schriemer, A. E. Bailey, and D. A. Weitz, Phys. Rev. E **52**, 3106-14 (1995).
[10] R. L. Weaver, J. Acoust. Soc. Am. **71**, 1609 (1982); Hennino et al., Phys. Rev. Lett. **86**, 3447 (2001).
[11] J. H. Page, P. Sheng, H. P. Schriemer, I. Jones, X. Jing, and D. A. Weitz, Science **271**, 634 (1996).
[12] A. A. Chabanov, M. Stoytchev, and A. Z. Genack, Nature **404**, 850 (2000).
[13] P. B. Allen, J. L. Feldman, J. Fabian, and F. Wooten, Philos. Mag. B **79**, 1715 (1999).