measurement (such as a study of the oscillation of a cylindrical cavity containing SPH), the *b* state will show a much smaller effective superfluid density and will produce a lot more damping than the *a* state.

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[6]The representation $\zeta = \exp(-i\theta\hat{\nu}\cdot\vec{J})\zeta_0$ also implies that $v_{si} = (m\hbar/M)\varphi_1\cdot\nabla_i\hat{\varphi}_2$ for all j, $m \neq 0$, where $\hat{\varphi}_1 + i\hat{\varphi}_2 = R(\hat{\nu},\theta)(\hat{x}+i\hat{y})$. The linearized hydrodynamics of the $S=\frac{1}{2}$ Bose fluid is discussed by B. I. Halperin, Phys. Rev. B 11, 178 (1975). The present definition of v_s reduces to the one therein when $\hat{l}$ becomes uniform.

[7]In ^{3}He-*A*, $\vec{g}$ contains terms proportional to $\nabla\times\hat{l}$. These terms are absent here because of the rotation symmetry in spin space.

[8]Away from the Ginzburg-Landau region, symmetry requires that, when $\hat{n}=\hat{z}$

$$F_G = \tfrac{1}{2}\rho_s v_s^2 + \tfrac{1}{2}\tilde{K}(\nabla_i\hat{l}_j)^2 + C\hat{z}\times\hat{l}\cdot(\vec{v}_s\cdot\nabla)\hat{l},$$

but places no constraints on the coefficients. The last term will produce a stronger (linear) instability.

[9]The family $\zeta^+(\vec{r},t) = (\sin\pi t/2,\ \exp(-iM\vec{u}\cdot\vec{r}/\hbar)\cos(\pi t/2))$ reduces the energy F_B+F_G monotonically as $(\frac{1}{2}K|\Psi|^2u^2 + M\Delta)\cos^2(\pi t/2) - M\Delta$, as t varies from 0 to 1.

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[11]The expression of $\nabla(f\zeta)$ indicates that only the sum $\vec{v}_s + \vec{w}$ is relevant. The current $\vec{g}$ does not depend on $\vec{v}_s$ and $\vec{w}$ separately. Since f is static, all the dynamics can be absorbed in $\vec{v}_s$, with $\vec{w}$ treated as a static background.

[12]For the ideal gas ($H_{1/2}$ with $V=0$) it can be shown that $C=0$ at $T=0$.

Tortuosity and Acoustic Slow Waves

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The experimental measurements of tortuosity of porous structures using either the acoustic index of refraction of superfluid ^{4}He or the electrical conductivity are shown to agree with each other. This and other measured parameters are used to calculate directly the acoustic speeds of water-saturated, fused-glass-bead samples; there are no adjustable parameters and agreement with experiment is excellent. The dependence of tortuosity on pore volume fraction, φ, is discussed.

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In this Letter we consider the acoustic and electrical properties of porous, fluid-saturated, fused-glass-bead samples (Ridgefield Sandstone) which have the unusual property that they support two distinct longitudinal acoustic modes.[1] The class of porous materials being considered is characterized by the unique topological property that the fluid and solid components each forms its

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own percolating, infinite cluster. The theoretical development which describes this longitudinal double-mode behavior, while preserving the unique topology of the system, is due to Biot.[2] The Biot theory has been successfully applied to various problems including fourth sound in a superfluid/superleak system,[3] pressure diffusion through porous media,[4] slow waves and the consolidation transition,[5] and the elastodynamics of gels.[6] In addition, there have been attempts to describe the acoustic properties of other porous media, typically sediments and sedimentary rocks,[7] but in these cases the most crucial aspect of the theory, the existence of a second "slow" compressional mode, was not observed experimentally. We demonstrate in this Letter, for the first time, that it is possible to independently measure all necessary input parameters of the theory at least in the high-frequency limit of the theory. We can thus make a successful comparison between theory and experiment which is meaningful only because all the modes predicted by the theory are measured experimentally. In previous articles[8] Berryman and Dutta obtained good agreement on similar samples by invoking additional theories to calculate those parameters; in this Letter we wish to demonstrate that this is not necessary.

We experimentally demonstrate, for the first time, the rigorous theoretical result that independent measurements of the tortuosity of the pore space (α) from the acoustic index of refraction of superfluid ^{4}He (n) and from the electrical conductivity of the pore space (σ) agree with each other. With the measured values of α and of the acoustic speeds of the dry samples, we calculate, with no adjustable parameters, the speeds of the fast longitudinal, slow longitudinal, and transverse waves in the water-saturated samples. These calculated speeds are in excellent agreement with our measured values.

The parameters of the Biot theory are α (the tortuosity), φ (the pore volume fraction), ρ_f and ρ_s (fluid and solid densities), K_f and K_s (fluid and solid bulk moduli), K_b and N (bulk and shear moduli of the dry sample). That is, the speeds of the compressional and shear waves in the dry sample are $V_L = [(K_b + \frac{4}{3}N)/(1-\varphi)\rho_s]^{1/2}$ and $V_T = [N/(1-\varphi)\rho_s]^{1/2}$, respectively.

The way in which the wet speeds (speeds of the fluid-saturated samples) depend on the various parameters is discussed in detail in Ref. 5. In particular, if the porous frame is much stiffer than the fluid ($K_b, N \gg K_f$) the phase velocity of the slow compressional mode is simply $V_f/\sqrt{\alpha}$, where $V_f = (K_f/\rho_f)^{1/2}$ is the speed of sound in the fluid. Moreover, if the viscous skin depth, $(2\eta/\rho_f\omega)^{1/2}$, is much smaller than a characteristic pore size, then the tortuosity, α, is real valued, greater than 1, and dependent only on the pore geometry; in this limit the slow wave is a wave predominantly in the fluid but with a speed renormalized down by the twisting, tortuous pore space. This mode was first reported by one of us on water-saturated fused glass beads.[1]

However, as was shown in Ref. 3, fourth sound in a superfluid/superleak system is the paradigm of the slow wave. The viscous skin depth of the superfluid is identically zero at all frequencies (the shear viscosity of the superfluid component is identically zero), and most solids are so stiff that the approximation $V_{\text{slow}} = V_f/\sqrt{\alpha}$ is accurate to 1 part in 10^4, typically. Thus the tortuosity is related to the index of refraction of fourth sound (n) by $\alpha = n^2$. Because the mode is essentially unattenuated, a fourth-sound measurement is seen to be a very sensitive way of measuring α on a given sample. The tortuosity is also related to the hydrodynamic drag parameter λ or χ by $\lambda = \chi = 1 - \alpha^{-1}$ (see Ref. 9 for a discussion).

In addition, α can be measured by purely electrical means. If the solid is insulating and the fluid has a conductivity σ_f, then the porous fluid sample has a conductivity σ which is proportional to σ_f, i.e., $\sigma = F^{-1}\sigma_f$. Brown[10] showed that $\alpha = F\varphi$. (Actually, for a rigid, nonconducting solid the relationship $n^2 = F\varphi$ is a rigorous theorem, known to Lord Rayleigh[11]—a simple derivation is given in Ref. 9—and is now generalized to the cases when the solid is compressible.)

The Ridgefield Sandstone samples are made of glass beads, whose diameters are in the range 177–210 μm, and are fused in an oven above the softening temperature.[12] The length of time in the oven determines the degree to which the porosity (φ) decreases from its initial value of 38% corresponding to dense random packing of hard spheres. A 4-in.-diam disk (typically $\frac{1}{2}$ to 1 in. thick) with plane and parallel faces is prepared. The dry acoustic speeds are measured, from which K_b and N are deduced. The sample is vacuum impregnated with water and the three wet speeds are measured by using a broadband pulse technique (described previously[1,5]) centered at 0.5 MHz. At this frequency, the viscous skin depth is about 1 μm, small enough to put us in the high-frequency limit of the theory.

A cylindrical plug, 0.250 in. in diameter by

1.225 in. long, is taken from the center region. The index of refraction (n) is measured on the ^{4}He-saturated plugs inserted into a cylindrical cavity by using an acoustic resonance technique described previously.[13] At each temperature the ^{4}He is at its vapor pressure. Our criteria for identifying the slow wave are that we observe at least four equally spaced plane-wave resonances which have the correct temperature dependence. In point of fact, the pore sizes are so large that the normal component is essentially unlocked and the modes follow a first-sound temperature dependence (the viscous skin depth of the normal component is about 1–5 μm over the range of temperature and frequency considered here); as long as the temperature dependence is known, this does not affect our results because first sound and fourth sound tend to the same limiting speed as $T \to 0$ (in practice, for $T \leq 1.2$ K).

The porosities of the cylindrical plugs were measured by using the standard three-weight (wet, dry, and buoyant) method. The sample volumes, calculated from these three weights, agree with the geometrically measured volumes. Moreover, the calculated grain densities are all in the range $\rho_s = 2.495 \pm 0.005$; this is the value we use in the theory, below. Thus we conclude that the fusing process has created little occluded porosity.

Finally, the electrical conductivity was measured on the identical cylindrical plug on which the ^{4}He measurement was made by saturating the sample with saline solutions. The actual measurements were done with a two-electrode cell using an ac bridge technique[12]; the electrodes were reversible Ag-AgCl plates and the conductivities were seen to be frequency independent over the range 100 Hz to 100 kHz. The conductivity was measured with four different solutions covering a range in conductivity from 0.0559 $(\Omega\ \mathrm{m})^{-1}$ to 9.823 $(\Omega\ \mathrm{m})^{-1}$. A straight-line fit to the data (σ vs σ_f) was made with R^2 values typically greater than 0.9998. In all cases this straight line extrapolated very nearly through $\sigma = \sigma_f = 0$; the worst-case intercept was $\sigma(\sigma_f = 0) = 0.021$ $(\Omega\ \mathrm{m})^{-1}$. The slope of this line is $1/F$.

We have plotted the values of α (acoustical and electrical) against the porosities of these samples in Fig. 1. We see that there is excellent agreement between these two measurements of this one parameter. This experimental verification of the rigorous theorem has apparently never been done before. The power of this equivalence is that one now has two complementary techniques for measuring the same microgeometric parameter: Obviously, electrical measurements are useless if the solid is itself a conductor.

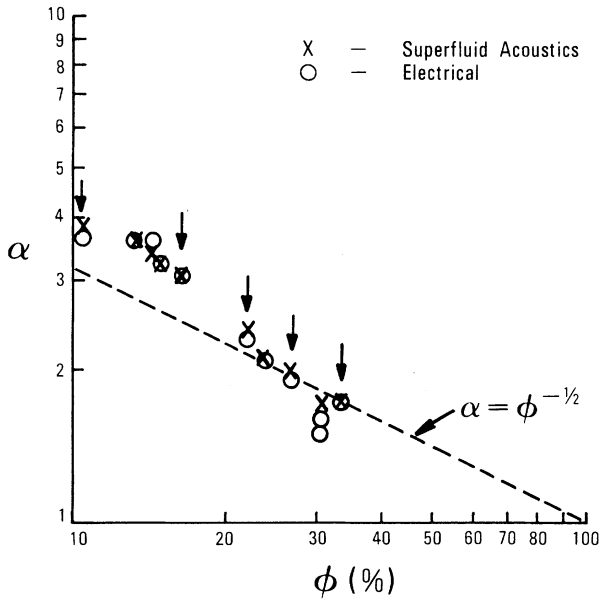

FIG. 1. Values of the tortuosity of fused-glass-bead samples deduced acoustically with superfluid ^{4}He and deduced electrically by using saline water. The dashed line is the prediction of Sen, Scala, and Cohen (Ref. 12). The arrows indicate those samples used in the analysis of water-saturated speeds (Table I). There are two different samples of 30% porosity.

Previously, Sen, Scala, and Cohen[12] developed a "self-similar" model which predicts $\alpha = \varphi^{-\beta}$ where β is a constant whose value depends on grain shape. Basically, the idea is that the porosity forms a kind of correlated percolation problem with the percolation threshold, p_c (i.e., φ_c), equal to zero, and β is essentially the conductivity exponent. A random array of needles gives $\beta = \frac{2}{3}$ and this was in substantial agreement with the existing data on packed-powder superleaks.[9] A random array of spheres gives $\beta = \frac{1}{2}$ and this prediction, $F = \varphi^{-3/2}$, was in perfect agreement with the measured electrical conductivity of similarly prepared samples[12] over a range of porosity $\varphi = 0.03$ to 0.38. We are still trying to resolve the small but measurable differences between the two sets of seemingly identically prepared samples. Note that all values are substantially larger than predicted by the empirical rule,[9] $\alpha = 2 - \varphi$, but it is still ambiguous how α behaves in the limit $\varphi \to 0$.

We now calculate the water-saturated wet speeds and compare against the experimental data; this is the main result of the paper. For the sake of

definiteness we choose α equal to its value given by the superfluid data. We use $K_s = 4.99\times10^{11}$ dyn/cm^2 (Ref. 4). We assume $\rho_f = 1.0$ g/cm^3 and $K_f = 2.25\times10^{10}$ dyn/cm^2 appropriate to water. In Fig. 1 we have indicated those samples for which we have acoustic data on the water-saturated large disks. The comparison of theory versus experiment is presented in Table I; the agreement is seen to be excellent thus giving the first direct experimental evidence for the validity of the Biot theory.

However, we hasten to point out that all our samples are very nearly in the stiff-frame limit ($K_b, N \gg K_f$). The speeds of the shear and of the fast compressional waves are not very sensitive to water saturation (the dry speeds are included in the last two columns of Table I, in parentheses). A more stringent test of the theory, then, is to compare *differences* in wet and dry speeds for the shear and the fast compressional waves. Here, there is good, general agreement although the differences in velocities are comparable to (or less than) our errors ($\pm 3\%$). Similarly, the speed of the slow wave in the stiff-frame limit, $V_f/\sqrt{\alpha}$, is included in Table I in square brackets; although this last expression gives a reasonable approximation to the slow wave speed, it is clear that the full theory gives a much better description of the acoustic properties, particularly for the higher-porosity samples. It is also clear that the tortuosity (α) is the key parameter governing these fluid-based slow waves. As a point of reference, the speeds in water, $V_f = 1.5$ km/sec, and in superfluid at $T = 0$, $V_f = 0.24$ km/sec, differ by an order of magnitude, but the slow waves have the same α; we could have predicted the superfluid speeds from the water-saturated data had we wished.

There is an appreciable, and apparently systematic, disagreement between theory and experiment for the water-saturated slow wave speeds of the samples with low porosity. This is probably due to the collapsing of the pore sizes such that viscous interactions become important. Indeed, these pulses are severely attenuated and broadened and the "arrival time of the pulse" is ambiguous. There are means of incorporating viscous damping[2] but they involve (a) additional and unjustified assumptions about the frequency dependence of the viscous drag force between fluid and solid, and (b) additional adjustable parameters. We feel that there is little to be gained from forcing an uncertain theory of the corrections into agreement with experiment by adjusting the parameters therein.

To summarize, (1) we have experimentally demonstrated the equivalence of acoustic and electrical means of measuring the tortuosity of a porous solid, thus making them complimentary techniques. Bulk superfluid ^{4}He is so well understood that it can now be used as a probe of the physics of disorder. (2) For the fused-glass-bead samples considered here, α appears to depart somewhat from the $\varphi^{-1/2}$ behavior reported earlier. (3) Measurements of the dry speeds and of the tortuosity have enabled us to accurately predict

TABLE I. Comparison of theoretically calculated speeds of sound for water-saturated, fused-glass-bead samples with the experimentally measured values. The input data are the dry speeds, listed in parentheses, and the tortuosity α, deduced from the superfluid ^{4}He saturated data. For comparison, the theoretical result for an infinitely rigid frame, $V_{slow} = V_f/\sqrt{\alpha}$, is given in square brackets. All speeds are in kilometers per second.

Porosity φ (%)	Tortuosity α	Slow theory	Slow expt.	Fast theory	Fast expt.	Shear theory	Shear expt.
33.5	1.75	1.01 [1.13]	0.99	3.23 (3.10)	3.19	1.75 (1.82)	1.68
26.6	2.00	0.97 [1.06]	0.94	3.89 (3.83)	3.98	2.20 (2.28)	2.21
21.9	2.40	0.89 [0.97]	0.88	4.35 (4.32)	4.60	2.57 (2.65)	2.57
16.2	3.02	0.81 [0.86]	0.70	4.82 (4.84)	4.83	2.74 (2.81)	2.68
10.5	3.84	0.71 [0.77]	0.58	5.17 (5.16)	5.15	3.04 (3.09)	2.97

the water-saturated speeds with no adjustable parameters. (4) The Biot theory is seen to effectively cut in half the problem of understanding acoustic propagation in porous media. It now becomes possible to focus on theories of the individual parameters, as has already been done, here, for the tortuosity, α.

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Method for the Exact Solution of a Nonlinear Diffusion-Convection Equation

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For a prescribed adsorption-desorption equilibrium maintained locally through a permeable solid, the concentration of a chemical substance is governed by the diffusion-convection equation $\partial c/\partial t = (D\nabla^2 - \vec{v}\cdot\nabla)[c/(1+K^{-1}c)]$ in which $c/(1+K^{-1}c)$ is the free concentration of the substance. Solutions of this nonlinear equation are shown to be related analytically to solutions of the elementary linear diffusion equation. This remarkable correspondence is utilized to obtain exact solutions to the nonlinear diffusion-convection equation.

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Consider a homogeneous permeable solid filled with a fluid which contains a chemical substance of concentration $c = c(\vec{x},t)$. Suppose that the solid microsurfaces adsorb a fraction of the chemical substance and leave a local free concentration $c/(1+K^{-1}c)$ in the fluid at adsorption-desorption equilibrium,[1] where K is a prescribed constant. With the adsorption-desorption processes relatively rapid and their equilibrium maintained locally, the total concentration c may change as a result of diffusion and convection of the free concentration, and one obtains the governing equation

$$\partial c/\partial t = (D\nabla^2 - \vec{v}\cdot\nabla)[c/(1+K^{-1}c)], \quad (1)$$

where D ($\equiv$ const) is the diffusivity of the chemical substance and $\vec{v}$ is the local convective flow velocity of the fluid. Equation (1) is the diffusion-convection analog of the Langmuir-Hinshelwood (Michaelis-Menten) rate expression featured in catalytic[2] and enzymatic[3] kinetics.

By introduction of the dimensionless dependent variable $\theta \equiv (1+K^{-1}c)^{-1}$, (1) takes the form

$$\partial\theta/\partial t = \theta^2(D\nabla^2\theta - \vec{v}\cdot\nabla\theta). \quad (2)$$

For the special case $\vec{v}\equiv 0$, (2) becomes the equation for nonlinear heat conduction in solid hydrogen,[4] where θ (also positive and less than or equal to unity) is a dimensionless thermal variable. The author has shown that one-dimensional solutions to the latter nonlinear heat-conduction equation are related analytically to solutions of

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