Third Sound in ^{4}He Adsorbed on Nuclepore

J. M. Valles, Jr., D. T. Smith, and R. B. Hallock
Laboratory for Low Temperature Physics, Department of Physics and Astronomy, University of Massachusetts, Amherst, Massachusetts 01003
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Measurements of the velocity of third sound C_3 in ^{4}He films adsorbed on Nuclepore filter material with and without pores have been made and reveal striking structure as a function of film thickness for the porous case. In the absence of capillary condensation the data are understood in terms of a model which predicts the porous index of refraction as a function of coverage. It is likely that the techniques employed will be a useful alternative to the Brunauer-Emmett-Teller method for the determination of surface areas. For helium film coverages above those necessary for capillary condensation a fast propagating mode with speed $v \sim C_3^{1/2}$ is observed.

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The behavior of fluids in porous media and the adsorption of fluids onto porous substrates has attracted serious attention from a wide spectrum of workers. Porous media of various sorts have also provided a medium in which to study the effects of restricted dimensions on the properties of ^{4}He and the superfluid transition. For many of these studies the substrate of choice has been powders,[1,2] fibrous filter material, or Vycor glass.[3] In all such cases the surface of the substrate material and void structure is not particularly well defined. Nuclepore[4] represents an exception to this situation and it has been used to study the heat capacity[5] of ^{4}He and ^{3}He-^{4}He films of various thicknesses. For the present work we have selected Nuclepore as the substrate material and have studied the propagation of third-sound[6] waves in ^{4}He films adsorbed on the Nuclepore as a function of the ^{4}He film thickness.

The third-sound mode in ^{4}He films is analogous to a tidal wave on the ocean where the wavelength is long compared to the depth H of the ocean. For such a tidal wave the speed v is to good approximation $v=(fH),^{1/2}$ where f is the restoring force per unit mass due to gravity. In the case of third sound the propagation speed is $C_3 \approx (\rho_s f h/\rho)^{1/2}$, where ρ_s/ρ is the superfluid fraction in the film and h is the film thickness. For relatively thin films the restoring force is given by $f \approx 3\alpha/h^4$, where α is the van der Waals constant[7] appropriate for ^{4}He and the substrate material. For the case of ^{4}He on Nuclepore, we have taken[8,9] $\alpha = 50$ (layers)^3 K.

Although we are engaged in a study of disordered substrates using third sound in an effort to find evidence of localization effects,[10] the motivation for this particular work was the desire to utilize Nuclepore as a large-surface-area–small-volume substrate for simultaneous third sound and NMR studies of ^{3}He-^{4}He mixture films. For such work an understanding of the effect of the pores in the Nuclepore on the propagation of the third sound is important. Porosity and substrate surface imperfections[11] have long been known to reduce the speed of a propagating third-sound wave. The reduction in wave speed is generally characterized by an index of refraction n, where n is defined to be the ratio of the speed of the wave on a smooth surface to that on a rough surface of the same material, $n = C_s/C_R = \tau_R/\tau_s$, where $\tau_{R(s)}$ is the third-sound time of flight on the rough (smooth) surface.

For the present work we have made simultaneous studies of the third-sound time of flight on two samples of polycarbonate Nuclepore material. One sample was virgin, and the other had pores with nominal 0.2-μm-diam holes of the general shape[12] shown in Fig. 1 and discussed in the caption. This particular Nuclepore choice maximizes the total surface area per sheet of material and nominally has 3×10^8 perforations per square centimeter. The Nuclepore substrates were housed side by side in a brass chamber located at the end of a cryostat insert of generally standard design. Measurements of the vapor pressure inside and outside the chamber allow a determination of the ^{4}He film thickness on the Nuclepore material through use of a Frankel-Halsey-Hill isotherm.[7] Third sound is generated in the ^{4}He film by the heating of Ag strips which were evaporated directly onto the surface of the Nuclepore. Typically, single-cycle, clamped-sine pulses are applied to the Ag driver at a repetition rate of 14 Hz. Third-sound pulses are detected and their times of flight measured by observation of temperature changes in an evaporated Al strip film, biased at its superconducting transition temperature, located a known distance $l = 0.64$ cm away from the Ag driver. Signal averaging of the Al bolometer output is necessary to optimize the visibility of the detected signals. To facilitate the measurements both substrates were located in the common vacuum chamber so that there would be no question that measurements on the two substrates were taken under identical conditions of chemical potential.

In Fig. 2 we show the index of refraction determined in this work at $T = 1.40$ K over the film thickness range $3.5 \lesssim h \lesssim 20$ atomic layers displayed as $n = \tau_R/$

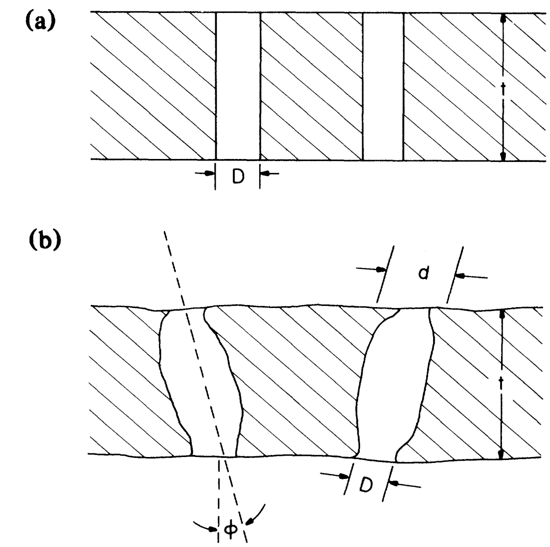

FIG. 1. Schematic illustration of the structure of the nominal $D = 0.2$-μm-pore polycarbonate Nuclepore filter material. The aspect ratios of the pores are greatly enhanced for clarity in both (a) and (b): (a) ideal cylindrical pore in $t = 10$-μm-thick substrate material; (b) schematic of the pore geometry. The angle ϕ for a given pore (Ref. 12) is distributed at random, $\phi \lesssim 34°$, and for our samples results in pore intersection; the substrate is well connected internally. The barrel shape (Ref. 12) is due to the etch process. The distortions from a cylindrical shape have been overdrawn to emphasize the necked ends and barrel shape.

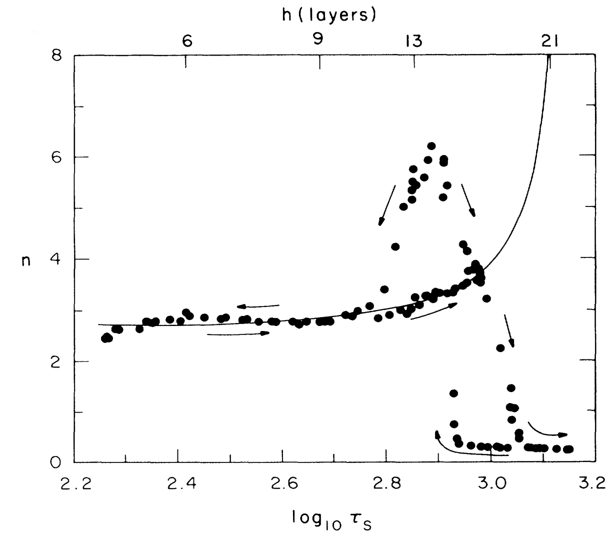

FIG. 2. The observed index of refraction n as a function of the time of flight $\log_{10}\tau_s(\mu\text{sec})$ observed on the virgin Nuclepore surface for $T = 1.40$ K. The curve is a prediction based on the general theoretical model developed in Ref. 16. The thickness scale is approximate (Ref. 13) and is provided solely to illustrate the general behavior of n with coverage.

τ_s vs $\log_{10}\tau_s$, where τ_s (τ_R) is the observed third-sound time of flight on the virgin (porous) Nuclepore. (Also shown in the figure is an estimate of the ^{4}He film thickness.[13]) The Kosterlitz-Thouless two-dimensional phase transition[14] was observed to be at the same thickness[13] $d_c^* = 4.0$ layers for the two substrates at $T = 1.40$ K (to within 0.1 layer) and was observed by the presence of a nearly abrupt vanishing of the third-sound[15] signal at d_c. We did not carry out high-resolution studies near d_c^* to examine for evidence of transition broadening. In Fig. 2 the index of refraction is observed to rise from a plateau of $n \approx 2.8$ at low coverages, exhibit hysteretic behavior near $h = 12$ layers, and then fall to a very low value beyond the region of hysteresis. The arrows on the figure indicate the evolution of the index of refraction for increases and decreases of the helium film thickness. The plateau and gradual increase of n at relatively low coverages can be understood in a simple way to be due to the reservoir of helium film in the perforations, the rise and hysteresis to be due to the approach to and presence of capillary condensation, and the low value of n at high coverage to be due to filled pores and a propagating mode of unexpectedly large velocity.

The index of refraction will differ from unity whenever a change in the flat-surface helium film thickness h produces a change in the volume $\Delta V(h)$ of helium trapped by a single scatterer, in this case, a pore. The calculation of the trapped volume may be simple, as in film present on the cylindrical wall of an ideal pore, or complicated, as in a partially capillary condensed pore. Cohen and Machta[10,16] and Guyer[16] have derived an approximate general expression for the index of refraction, $n = [1 + \gamma\partial(\Delta V)/\partial h]^{1/2}$, in a system with an areal density γ of identical scatterers in the absence of tortuosity.

For the simple case of perfect perpendicular cylindrical holes in a slab of material, we have $\Delta V = \frac{1}{2}(\pi d t h' - \pi d^2 h/2)$, where d is the diameter of the pore, t is the thickness of the substrate material, and $h' << d$ is the helium film thickness in the pores. Far from the capillary condensation limit, $\partial h'/\partial h \approx 1$ and the expression for the index of refraction for the case of cylindrical pores becomes $n_0 \approx [1 + \frac{1}{2}\gamma\pi d(t - d/2)]^{1/2}$. For our case there is a distribution of t values[17] with $t \gtrsim 10$ μm. Another approach[16] for the case of perfect cylindrical pores yields the somewhat more transparent expression $n_0 \approx (1 + A_p/2A_s)^{1/2}$, where A_s is the surface area of one face of the planar substrate material corrected for the presence of the pore openings and A_p is the total surface area of the pores. At low coverage in the presence of tortuosity ϵ one has[16] $n \approx n_0(1 + \epsilon A_p/2A_s)^{-1/2}$. With $\epsilon \approx 0.1$ we find $A_p/2A_s$ to be substantially larger than expected based on the nominal value for A_p. Previous Brunauer-Emmett-Teller (BET) measurements on 0.2-μm Nuclepore[5] have also observed an enhanced area. These present data reveal a trend for n to fall below this plateau at very small values of the film thickness. We do not understand this, although it may be related to small differences in ρ_s/ρ on the two substrates or to the effect of microscopic roughness. That it has its origin on the perforated substrate is likely; a weak inflection point is visible in the perforated time of flight τ_R near $h \approx 5$ layers, just where n begins to fall with decreasing coverage.

Far from the capillary condensation limit the observed index of refraction bears a simple relationship to the enhanced area available to the helium film due to the pores. This should remain the case for rough or artificially contaminated[2] substrates as well. It is possible that this technique might prove useful as an alternative to the standard BET measurement for the determination of surface areas, particularly in situations where the surface area is relatively small.

As the film is thickened the film in the pores thickens faster than that on the surface of the substrate material. The thickness ratio h'/h is governed by chemical-potential equilibrium between the pores and the substrate, $h^{-3} \approx h'^{-3} + \sigma/[\alpha\rho(\frac{1}{2}d - h')]$, where ρ is the helium density and σ is the surface tension. This enhances the simple geometric effect of the index of refraction previously discussed and causes n to rise with an increase in h; n diverges as a function of film thickness at the capillary condensation transition in the pores. This predicted enhancement is shown for the case of uniform cylindrical pores with tortuosity in Fig. 2, the smooth curve. We have allowed d and γ to be adjustable subject to the constraint that at low coverage $n = 2.8$, and find for the curve shown that $\gamma = 3.5 \times 10^8$ cm^{-2}, $\epsilon = 0.11$, and $d = 0.46$ μm. The value of γ is consistent with scanning-electron-microscope measurements of our substrates. The larger than nominal value of d is perhaps understandable given the less than perfect internal shape[18] of the pores and the previous[5] observations of enhanced area on Nuclepore. We interpret the termination of the increase in n with increasing τ_s (i.e., with increasing coverage) with the premature onset of capillary condensation in the imperfect pores and subsequent appearance of the new mode mentioned above and discussed below. Were the situation ideal and the pores perfect noninteracting cylinders of uniform size, n might be expected to continue to rise as shown by the curve in Fig. 2. Increasing values of n with helium coverage have also been seen in packed powders[1] or powder-dusted substrates[2]; quite large values of n can sometimes be attained.

The observed hysteresis is apparently associated with the tendency for partially capillary condensed regions to remain so in spite of changes in the film thickness. Violent changes in film thickness or temperature can cause jumps from one hysteresis branch to another. Theoretical work by Saam and Cole[19] has shown that capillary condensed regions in perfect cylinders can be expected to exhibit hysteresis; such pores remain partially filled with ^{4}He as the film thickness is reduced below the capillary condensation limit. The width of our hysteresis region is in general agreement with expectations based on their theory. We expect that the specific structure of the hysteresis peak is related to details of the pore size distribution, internal roughness, and pore intersections.

We observe a propagating mode of unexpectedly large velocity on the porous substrate at the highest coverages where the pores are completely filled. The propagation speed is observed to be much faster on the porous than on the virgin material with $n \approx 0.25$. The dependence on thickness is weaker in this thickness range. In particular we observe that $\tau_R \sim \tau_s^{1/2}$. Thus, the speed of this mode scales as the square root of the virgin-substrate third-sound velocity. This is shown rather clearly in Fig. 3. As a result of randomness in ϕ, the pores intersect each other sufficiently often that it is very likely that they percolate laterally within the Nuclepore. Although we have no fully satisfactory model which explains this propagating mode, we believe it to be a combined surface-bulk disturbance.

We have reported measurements of the propagation of third sound in ^{4}He films adsorbed on Nuclepore. Index-of-refraction values substantially greater than unity are observed and understood on the basis of models from which the index of refraction can be easily calculated because of the relatively simple nature of

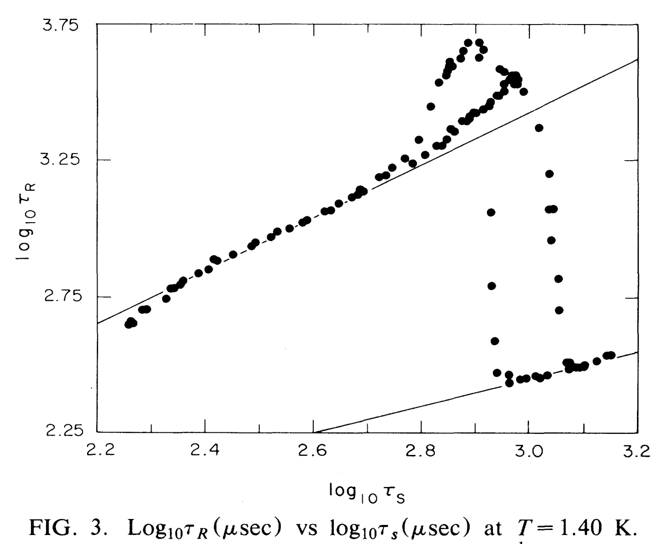

FIG. 3. $\mathrm{Log}_{10}\tau_R$(μsec) vs $\log_{10}\tau_s$(μsec) at $T = 1.40$ K. The solid lines are drawn with slopes of 1 and $\frac{1}{2}$ and illustrate clearly that $C_R \sim C_s^{1/2}$ for the higher coverages associated with filled pores. For lower coverages the slope of unity indicates that the dependence of the third-sound velocity on film thickness is the same on both the porous and the virgin substrates.

the porosity in the substrate. The large effect that these pores have on the third-sound velocity is the apparent origin of the low third-sound values in thin ^{4}He films recently reported by Noiray *et al.*[8] Third sound has been shown to be capable of determining tortuosity and surface areas and under some conditions may be an alternative to the standard BET technique. A fast and incompletely understood mode propagates in the presence of filled pores.

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[8]J. C. Noiray, D. Sornette, J. P. Romagnan, and J. P. Laheurte, Phys. Rev. Lett. **53**, 2421 (1984).

[9]The work of Ref. 8 with $\alpha = 50$ layers^3 K reports the simple form of the van der Waals potential α/h^3 to be valid over a wider thickness range than does Ref. 5 with $\alpha = 37$.

[10]Such effects have recently been predicted for helium films on disordered substrates. See S. M. Cohen and J. Machta, to be published.

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[13]This approximate thickness scale was determined from the use of $h^3 = \alpha/(T \ln P_0/P)$ with (Ref. 8) $\alpha = 50$ (layers)^3 K. Here P_0 is the saturated vapor pressure of ^{4}He at temperature T and P is the vapor pressure in the chamber where the film thickness (on the flat surface) is h. Predicted values for τ_s based on the path length and on the above determined d values and $l = \tau_s C_s$, with $C_s^2 = fh\langle\rho_s\rangle/\rho$ $f = 3\alpha/h^4$, $\langle\rho_s\rangle/\rho = (\rho_s/\rho)(1-\beta/h)$, and $\beta = 0.5 + 1.13T\rho/\rho_s$, agree with measured values of τ_s over most of the thickness range to $\lesssim 5\%$. The expression for β is valid for glass; its use for Nuclepore results in uncertainty of a few tenths of an atomic layer in the connection between the approximate thickness scale and τ_s only at very low coverages.

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