Third sound in superfluid $^4$He films adsorbed on packed multiwall carbon nanotubes

Emin Menachekanian and Gary A. Williams
University of California, Los Angeles, CA 90095 USA
E-mail: eminm@physics.ucla.edu, gaw@ucla.edu

Abstract. Third sound propagation is observed with thin $^4$He films adsorbed on multiwall carbon nanotubes. At an average diameter of 12 nm and a length of several microns, the powder of nanotubes is lightly packed into a cylindrical resonator, with a resistor bolometer at the cylinder end to detect the temperature oscillations accompanying the waves. The lowest standing-wave mode in the cavity is excited by mechanical vibrations, with FFT analysis allowing measurement of the sound speed as well as the dissipation. A finite-size broadened Kosterlitz-Thouless onset transition is observed with increasing film thickness on the outside nanotube surfaces for temperatures between 1.3 and 1.7 K. At higher thicknesses capillary condensation becomes important, probably at connection points where the nanotubes touch. We have seen no clear indication of effects that might be attributable to the adsorption of helium on the inner surfaces of the nanotubes.

1. Introduction
The adsorption of superfluid films on carbon surfaces has been studied for a number of different bulk substrate types, including graphite foam (grafoil) [1, 2], carbon fibers [3], and HOPG graphite [4]. A number of interesting phenomena have been observed in these systems, including layer-by-layer growth of the film thickness, re-entrant superfluidity, and the 2D Kosterlitz-Thouless transition. We are carrying out studies on carbon nanotube substrates to investigate how the sharply reduced length scale of the nanotube radii affects these properties. We have previously studied third sound propagation in helium films on single-wall nanotube “ropes” of average radius 5 nm, where the nanotubes initially in solution were sprayed and dried onto a plastic surface, leaving a connected tangle of tubes with a thickness of about 10 microns [5]. The Q factor of the third sound in this geometry turned out unfortunately to be rather poor, at best of order 10, making detailed studies of the superfluid transition difficult. We believe the Q factor was degraded in this geometry because of the proximity of the tubes to the open vapor region above the plastic surface, though this is not entirely clear.

To restrict the vapor motion we have gone to a geometry of bulk packing of the nanotubes into a closed cavity in a plastic form. The data reported here were taken with multiwall nanotubes packed into a narrow cylindrical cavity, with the ends of the cavity closed with end caps containing a heater and a resistance bolometer to generate and detect the third sound. This proved to be successful in raising the third sound Q factor, to values as high as 500.
Figure 1. Third sound velocity and attenuation (Q factor) at 1.3 K (open and closed circles are runs on different days).

Figure 2. Third sound velocity and attenuation (Q factor) at 1.7 K.

2. Experiment

The nanotubes used in the present measurements are specified by the manufacturer [6] to have radii between 8 and 15 nm and length of about 1-2 microns, and these particular tubes were functionalized with COOH. The cylindrical cavity was formed by drilling a 6.35 mm hole through a Plexiglass rod 3.81 cm in length. The multiwall nanotubes were packed into this cavity with about 10 fills of 0.05-0.1 grams each, for a total of 0.73 g. After each fill the tubes are compressed by hand with a packing tool the same diameter as the cavity. Assuming a tube density of 2.1 g/cm$^3$ gives an average porosity of 0.71. Since the tubes remain conducting to low temperature, they are insulated from the heater and bolometer mounted on Plexiglass end plates by a layer of Nucleopore filter. Two different heaters were tried, one consisting of 40 Ω of resistance wire wound in a tight coil, and the other a thin layer of carbon paint of resistance about 1 KΩ. For unknown reasons neither of these were successful in generating a third sound signal, even at drive powers up to 100 µW where dc heating of the film became a problem. We found, however that we were able to generate signals by lightly tapping the cryostat with a hammer. The bolometer is a 200Ω Allen-Bradley resistor with one side of the case sanded off for thermal contact to the film. At low temperature the resistance increases rapidly, to nearly 100 KΩ, allowing detection of the oscillating temperature component of the third-fifth sound mode. The difference in the vapor pressure in the indium-sealed cell and in the helium bath is measured with a capacitive diaphragm (MKS Baratron) with a resolution of 10$^{-6}$ torr.

Figure 1 shows the measured third sound velocities and Q factors at 1.30 and 1.70 K, as a function of the vapor pressure in the cell. The resonant peaks are obtained by recording the free decay of the mechanically-generated oscillations with an FFT technique, averaged over 50-100 hammer taps. We only observed a single resonant mode (near 200 Hz at onset for 1.3 K), which
we assume is the fundamental mode, corresponding to a half-wavelength fitting into the length of the cell. With the mechanical excitation the next mode would be expected at three times the frequency of the fundamental, but the tapping apparently did not couple sufficiently to give observable signal at those frequencies.

The onset of observable third-sound propagation occurs at cell pressures near $p/p_0 = 0.40$ and 0.73 for the two temperatures, where the Q factor is initially fairly low, but then increases quickly with further filling. The onset thickness where we first observe a propagating signal at 1.3 K can be calculated as 3.07 layers, using the calculation of Ref. [5] which takes into account the effect of the cylindrical geometry on the van der Waals energy, and the surface tension. The calculation does not include, however, the nearly one additional layer due to the solid layers postulated in in Ref. [1], so our onset thickness could actually be closer to 4 layers. The same calculation for the 1.7 K data gives an onset thickness of 3.85 layers.

On metering in increasing amounts of helium the velocity increases to a maximum and then begins to decrease. This is an indication of a finite-size broadened Kosterlitz-Thouless transition [8, 9, 10], where now the diameter of the tubes is the limiting length [7]. The behavior is similar to that seen for the case of third sound adsorbed on alumina powder [8, 9], where the initial increase is due to the increasing superfluid density at the transition, and then the decrease due to the lowered van der Waals restoring force with increasing thickness. The degree of broadening is quite similar to that seen in Ref. [9], though this is difficult to quantify precisely since the temperature ranges do not overlap. We do not observe any obvious oscillations in the third sound velocity due to layering effects, as seen in Refs. [1, 4]. It is unclear with the highly curved nature of the nanotube surface that the helium film will still grow in distinct layers. It may also be that the range of tube diameters present in our sample could act to smear out such layering, or that these temperatures are too high to resolve the effect.

At higher fills closer to saturation the third sound velocity reverses direction and increases rapidly, reaches a maximum, and then drops just as rapidly. We believe this is the point where capillary condensation begins to occur at points where the nanotubes touch; similar behavior is seen in packed powders [11]. Though difficult to see in Fig. 1 (since points overlap), at the very highest fill the sound velocity begins to rapidly increase once again, which is likely from entire pores filling in and the liquid compressibility (fourth sound) becoming appreciable.

Figure 3 shows a helium adsorption isotherm at 1.30 K for a sample of nanotubes similar to those used in the third sound measurements, but now packed into a different annular geometry, 4.0 cm in outer diameter and 8.7 mm wide. These are again multiwall tubes 8-15 nm diameter, but without functionalization [12]. An annular packing tool is used to pack two layers of tubes by hand to a total depth of 2.56 mm, resulting in a porosity of about 0.86. The rapid rise and leveling in the fill at the lowest pressure presumably marks the completion of the first solid layer on the tubes, though it seems to have taken a relatively large fraction of the total fill (which is about 2200 mm Hg pressure change in the $^4$He gas fill tank). Another possibility is that this rise could also reflect a filling of the inside of the nanotubes, which with an estimated diameter of 3-5 nm could be accessible to the helium if the nanotube ends are not capped. We do not see any indication of superfluidity in this regime; if the filling does occur, superfluidity would probably require lower temperatures for helium confined to such small length scales. In the region of the superfluid onset that we do see at $p/p_0 = 0.40$ (shown by the arrow) the isotherm seems to be well described by the standard van der Waals theory. The dashed curve in the isotherm is a fit to a power law, and the resulting exponent is 0.33, as expected from the $z^{-3}$ variation of the van der Waals energy for thin films. There does not seem to be any visible layer completion effects in the isotherm except the initial one, unlike the layering steps seen in Ref. [1]. However, those only became readily visible at lower temperatures than ours; we are currently extending our measurements to lower temperatures where such changes in the third sound velocity may be more noticeable.
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[12] In preliminary third sound measurements with this cell we have found no apparent difference between the functionalized and unfunctionalized nanotubes.

Figure 3. Adsorption isotherm on multiwall carbon nanotubes at 1.30 K. The arrow shows the onset point for third sound.