Investigating the Lapse in Third Sound Signal from Superfluid ^{4}He Adsorbed on Carbon Nanotubes

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Abstract

Two theoretical models are developed and tested to understand a particular mode of superfluid vibration called third sound. In particular we are trying to explain a brief lapse in third sound in early ^{4}He film development on a carbon nanotube substrate. We use a resonant cavity of nanotubes at 1.3 K and introduce ^{4}He gas. Using a variable-frequency heat pulse and a thermometer, we utilize the temperature waves generated by the superfluid oscillations in order to detect third sound. The experimental data consists of resonant peaks, representing superfluid oscillation, at various film thicknesses. There are two goals within the theoretical work: accurate calculation of film thickness from ^{4}He gas pressure readings, and mathematical models for two qualitative explanations. These two hypotheses—quasi-solidification and nanotube filling—are compared against experiment. We have found that quasi-solidification is a good predictor of the lapse in third sound. More data is needed to more firmly support this conclusion, and several experimental and theoretical improvements are proposed. If further evidence points towards the quasi-solidification model, it could become part of the explanation of superfluid behavior in thin films.

Introduction

The intrinsic properties of superfluid ^{4}He lead to several novel sound modes, some of which have well-formulated theories that are experimentally confirmed. The following research was conducted to more clearly understand a particular mode called third sound. In particular, this work aims to experimentally confirm and theoretically explain a brief lapse in third sound as thin films of ^{4}He build up on a carbon nanotube substrate. The third sound phenomenon is based on several physical facts:

- According to Landau's two-fluid model, the superfluid phase consists of two components, a normal fluid and a superfluid, which act independently.
- A superfluid has zero viscosity.
- A superfluid acts as a thermal superconductor. It flows frictionlessly to eliminate temperature gradients.
- Temperature moves through a superfluid as a wave. (In a normal fluid, it spreads diffusively.)

[1]

Third sound occurs on very thin films of liquid helium. These films are created by the van der Waals potential, which is strong at close range. The vdW force is the dipole-dipole electric attraction that forms between ^{4}He gas and a solid surface (called the substrate). Third sound occurs when this film is formed at a temperature below 2.18 K, and is disturbed by a temperature gradient. A thermal pulse will cause the superfluid component to propagate towards the heat source, while the normal fluid remains viscously clamped to the surface. This surge will lead to peaks of the superfluid component. These cold, superfluid-dense peaks will be restored through the vdW attraction, and through the nature of the superfluid which now flows towards the warmer troughs. [1] The resulting thickness and temperature waves—third sound—can be measured using a thermometer.

Third sound has been studied and theorized on flat substrates, but there is not yet a comprehensive understanding of this behavior on cylindrical geometry. We are working towards a complete theoretical model for very thin ^{4}He films adsorbed on carbon nanotubes. There are two goals in this theoretical work:

1. Accurately calculate film thickness based on experimental cell gas pressure as ^{4}He film builds on the nanotube substrate.
2. Explain the loss and re-entrant behavior of the superfluid third sound signal found experimentally (Figure 1).

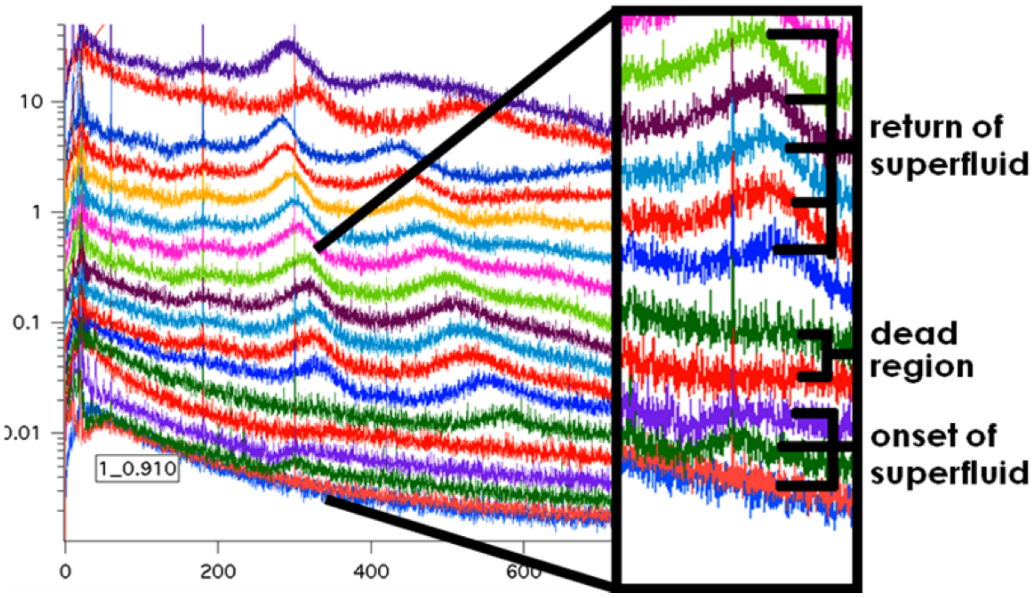

Figure 1. A lapse in third sound signal in early layers of superfluid film

In fact, achieving the first goal is the key to achieving the second goal, as will be explained later in the paper.

Methods

The carbon nanotube substrate was created by airbrushing multi-walled carbon nanotubes of 8-15 nm diameter in a rectangular region [2]. We expect that third sound will resonate overall along the length of the rectangle, as a significant fraction of the nanotubes are aligned in this direction. The nanotube substrate is placed within a plexiglass experimental cell. (Figure 2)

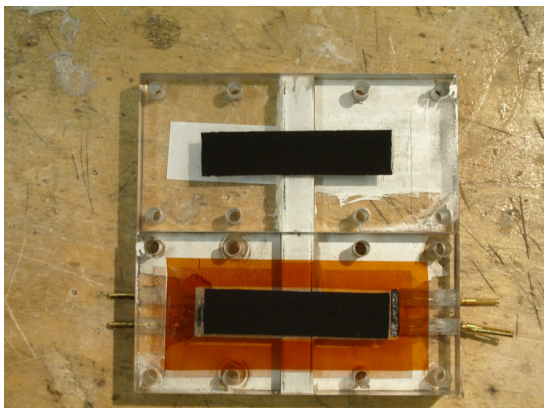

Figure 2. Experimental cell sprayed with carbon nanotubes (black rectangle)

We utilize the temperature waves generated by the superfluid oscillations in order to detect third sound. A heater is used to generate third sound, and a thermometer is used to detect it. Each element is placed at opposite ends of the rectangle. Carbon paint serves as the heater, powered by a function generator that sweeps from 10 –1000 Hz. The heater generates standing temperature waves at some resonant frequency within this range. The waves are detected by 200 Ω Allen-Bradley resistor, which acts as a bolometer (variable resistance temperature detector) because its resistance rapidly increases upon cooling. The resistor is biased with 1 μA current to detect voltage changes. (Figure 3)

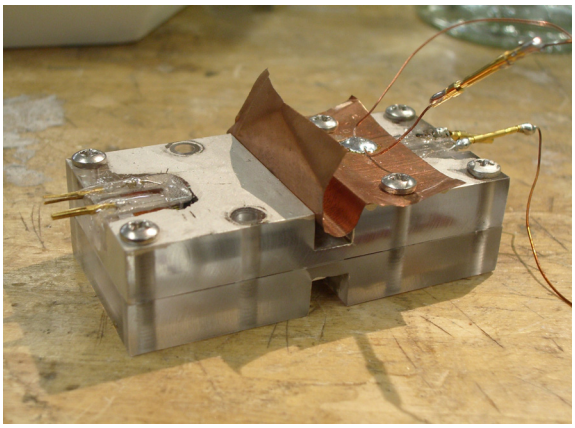

Figure 3. Closed experimental cell with heater and themometer on opposite sides

The entire experimental cell is placed in a vacuum-sealed chamber which is cooled to 1.3 K. Helium gas is slowly added, and layers of superfluid film begin to build on the nanotube surfaces through the van der Waals attraction. We keep track of superfluid layering by measuring the pressure inside this chamber. At each discrete film thickness, we sweep thermal pulse frequencies, occasionally hitting resonances. Resonance peaks signal superfluidity. Our data is analyzed using a Fast Fourier Transform (FFT) program in LabView . A representative graph is shown in Figure 4. Each line represents a different film thickness, increasing from bottom to top. Resonant modes are shown as peaks in the FFT profile.

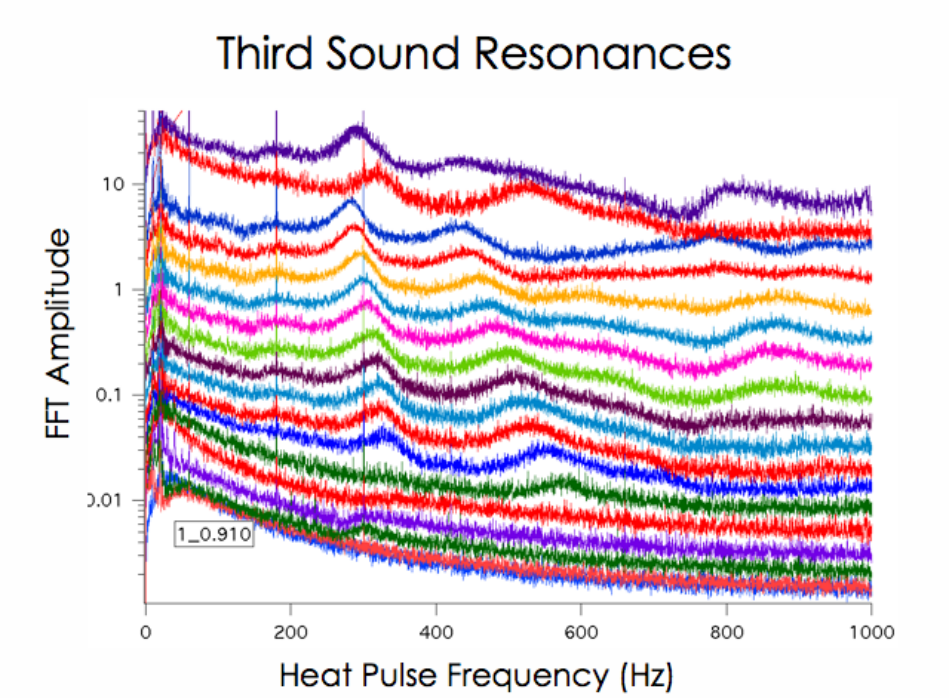

Figure 4. Superfluid onset, lapse in third sound signal, and re-entrant superfluidity from experimental run 32

A closer look reveals that the superfluid disappears briefly in the early stages of film buildup. (Figure 5)

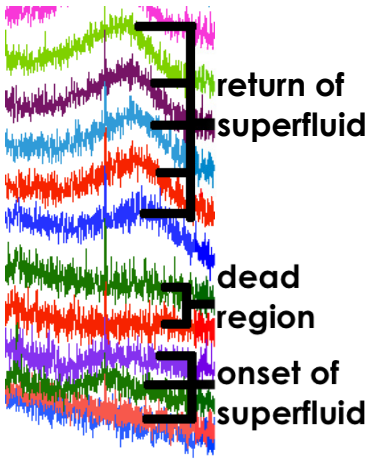

Figure 5. Detailed view of the disappearance of third sound signal as film thickness grows from bottom to top

Theory: Two Goals

1. Accurate Film Thickness

Film thickness on a flat substrate can be calculated using the Frankel-Halsey-Hill (FHH) equation, which is based on temperature (T), reduced pressure relative to saturated vapor pressure (P_0/P), and a van der Waals potential coefficient (α):

$$d = \left(\frac{T}{\alpha} \ln \frac{P_0}{P} \right)^{-1/3} \quad (1)$$

[3]

Experimental data has shown that the film is actually ≈1 atomic layer larger than predicted by this equation, so Cheng and Cole propose an adjustment to this equation. We now model the film as fluid outer layers with highly compressed inner layers called the pseudosubstrate (D_0). This pseudosubstrate has its own vdW potential acting on the liquid film (d'). The new equation modifies α by turning this number into a function of the liquid film (γ(d')):

$$d' = \left(\frac{T}{\gamma(d')} \ln \frac{P_0}{P} \right)^{-1/3} \quad (2)$$

where

$$\gamma(d') = \gamma^{a\text{-}ps} - \gamma^{a\text{-}a} + (\gamma^{a\text{-}s} - \gamma^{a\text{-}ps})(1 + D/d')^{-3}$$

(The γ terms are the new vdW coefficients, where the superscript refers to the two interacting components: a=adsorbate, ps=pseudosubstrate, and s=substrate)

[3] [8]

Figure 6 shows this correction over a range of pressures.

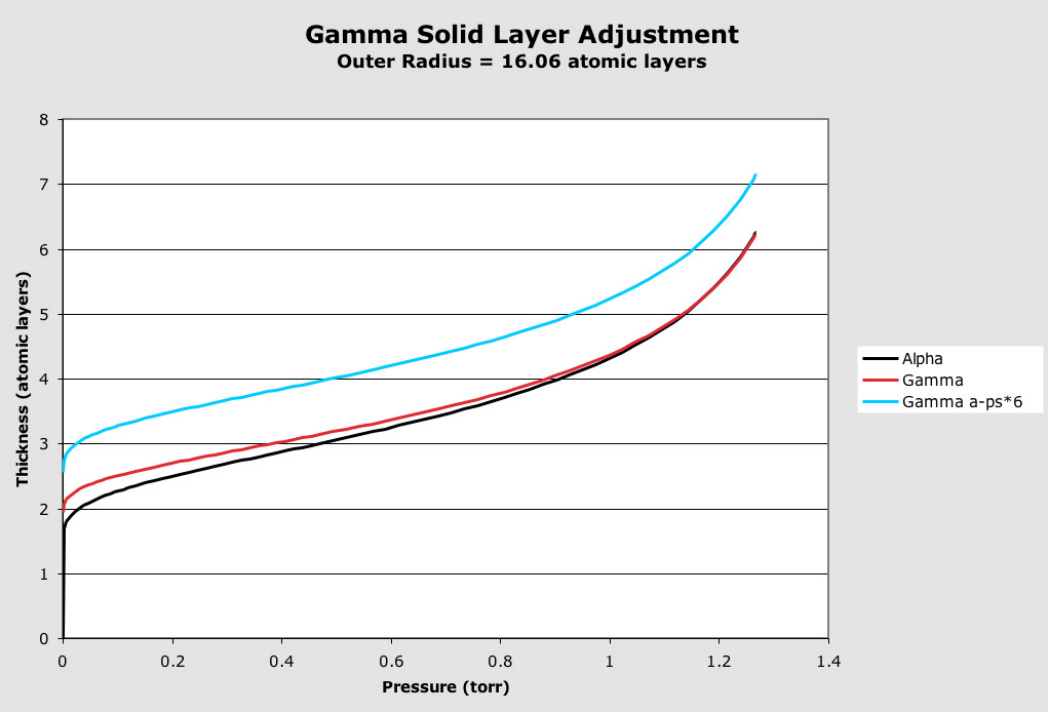

Figure 6. Pressure inside chamber vs. ^{4}He film thickness using original equation (α, in black) and improved equation ($\gamma(d')$, in blue)

In addition to this more precise model of the film's inner properties, we must also look at large-scale changes in the substrate's geometry, which is cylindrical rather than flat (Figure 7). Nanotubes of a 4 nm outer radius have a large curvature, which affects both the van der Waals force and the surface tension on the film.

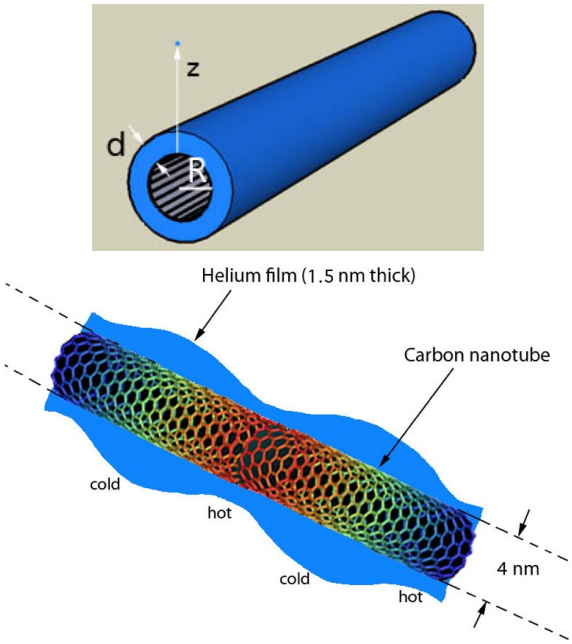

Figure 7. Geometric structure and illustration of third sound along nanotube subtrate

As Vo and Williams have shown, the van der Waals equation describing the potential energy between a Helium atom a distance z from a flat graphite substrate is:

$$U(z) = -\alpha/z^3 \quad (3)$$

where α is the vdW coefficient [4].
Since a helium atom near the surface of a cylinder is farther away from regions of the substrate that are curved away, the vdW force is reduced:

$$U(z) = \frac{18\pi\alpha R^2}{8(R+z)^5} F_1^2\left[\frac{5}{2},\frac{5}{2};2;\frac{R^2}{(R+z)^2}\right] \quad (4)$$

where R is the outer radius of the cylinder and F_1^2 is Gauss' hypergeometric function [5]. Figure 8 shows this reduction of vdW potential due to cylindrical geometry.

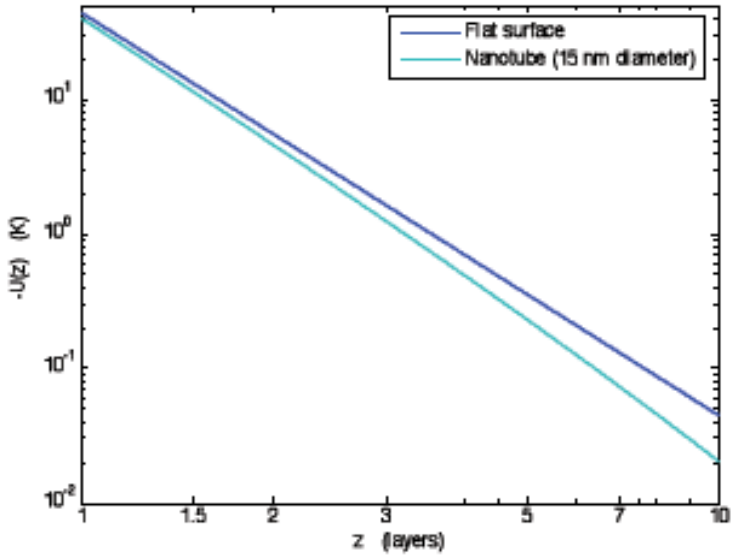

Figure 8. Difference in Van der Waals potential from flat and nanotube substrates (as a function of film thickness)

[4]
In addition to a reduced vdW force, the curved surface also leads to a dramatic increase in surface tension. Surface tension on the outside of a cylinder acts to decrease film thickness. Putting both of these factors together, we can find film thickness using the following equation:

$$k_B T \ln\left(\frac{p_o}{p}\right) = -U(d) - \frac{\sigma}{\rho(R+d)} \quad (5)$$

where d is film thickness, and the rightmost term is surface tension [4].

To summarize, we started with a basic equation for film thickness on a flat substrate, assuming uniform layering. An accurate film thickness is found by adjusting the vdW force and surface tension for cylindrical geometry, and by changing α into the function $\gamma(d')$ to account for solid inner layers.

2. Explanations for Lapse in Third Sound Signal

Quasi-Solidification

The first explanation comes from the characteristic van der Waals force that binds helium atoms to a surface. This potential is proportional to $1/z^3$, where z is the distance to the substrate [1]. Thus, it is strong at short range and falls of quickly with distance. The first few layers of film are so strongly bound that they become the solid pseudosubstrate mentioned earlier. The vdW potential has a great effect several layers beyond this, leading to moments of quasi-solidification at layer completion. Superfluid can move as third sound at the beginning of an atomic layer, but as this layer nears completion the atoms become crystallized by locking onto the carbon lattice structure. Third sound returns once the next layer begins.

Several experiments have shown that the lapse in third sound could be due to this layering effect. J. D. Reppy and P. A. Crowell have seen re-entrant behavior in torsion oscillator experiments conducted on grafoil. The period shift $\Delta P(0)$ (extrapolated to $T = 0$ K) is seen to vanish at the completion of the second layer. This behavior can be understood as a quasi-solidification of superfluid helium [6].

Layering effects have also been seen on graphite by G. Zimmerli, G. Mistura, and M. H. W. Chan. Using a graphite foam substrate, 2-d compressibility measurements showcased stiffening of helium film (corresponding to local minima of the compressibility) at the completion of each layer [3].

Using this theory, we would look at the film precisely at layer 4 (one the layers immediately beyond the pseudosubstrate which might get locked at completion).

Nanotubes Filling

The second explanation comes from the fact that film might build on the inside of the nanotubes in addition to the outer walls. Inside the tube we have a reversed curvature, which consequently reverses both the van der Waals adjustment and the surface tension term discussed earlier. We used a theoretical model developed by Saam and Cole, who calculated the thickness of a film formed within a porous substrate:

$$\ln\left(\frac{P_0}{P}\right) = 3\,\frac{\pi}{2}\,\frac{\alpha}{1.30\,R^3}\,\text{Hypergeometric2F1}\left[\frac{3}{2},\ \frac{5}{2},\ 1,\ \frac{(R-x)^2}{R^2}\right] + \frac{3.1278}{1.30\,(R-x)} \quad (6)$$

[7]

In comparison to equation (5), we see that the hypergeometric function is altered and surface tension is now positive.

Qualitatively, a helium atom on the inside of a nanotube will be closer overall to substrate material than a helium atom the same distance from the outside of the tube. In general, film will start building on the inside of the tube first. The reversed surface tension term means that the film will be thicker. As film grows, the curvature becomes more pronounced, and the film will grow exponentially until the tube fills. Figure 9 compares film thickness on the inside and outside of a cylinder.

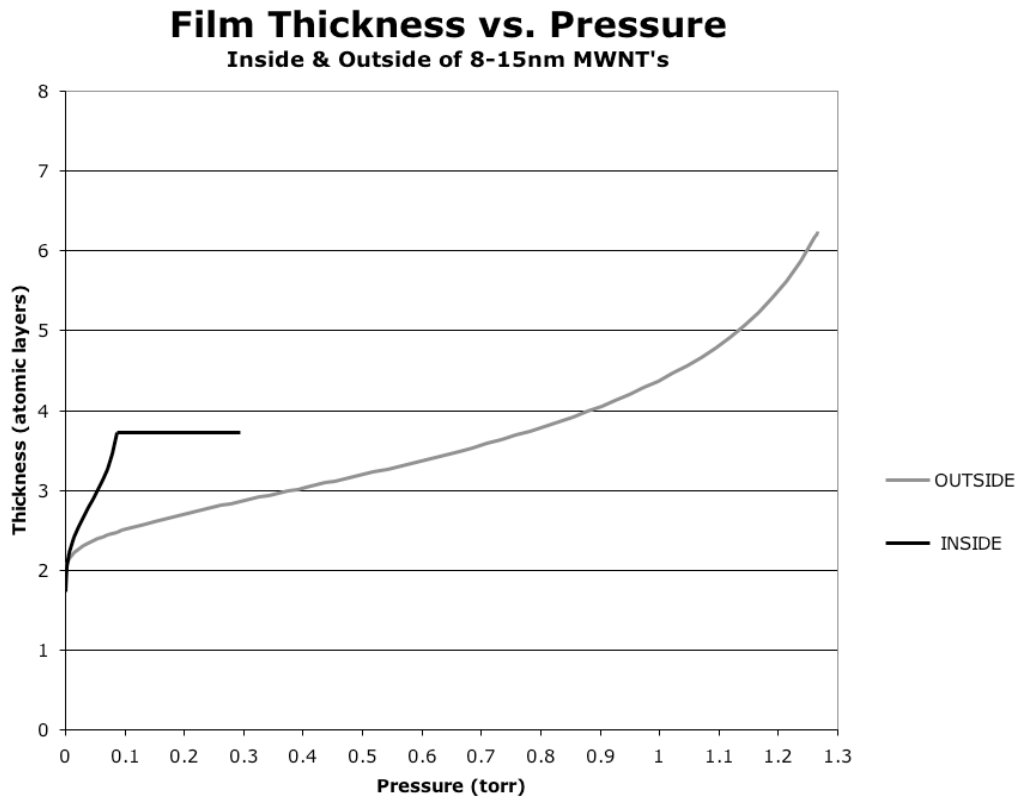

Figure 9. Film growth on the inside (black) and outside (gray) of a nanotube of 8-15 nm outer diameter, as a function of chamber pressure

A filled tube would explain the lapse in third sound signal. Third sound is defined as a two-dimensional thickness wave, and the filled tube is now a three-dimensional fluid. Now, additional film must now be built on the outside of the nanotubes. Third sound returns at this point.

Results and Discussion

To decide which (if any) hypothesis might explain the lapse in superfluidity, we must compare theory to experiment. Our theoretical calculations provide a particular chamber pressure where third sound might freeze. We then match this number to a particular pressure line in our experimental graph, and examine how closely it matches the region of third sound disappearance.

According to the quasi-solidification theory, the fourth layer is a reasonable region for the film to lock to the substrate lattice. Figure 10 shows that the corresponding pressure is about 0.5 torr.

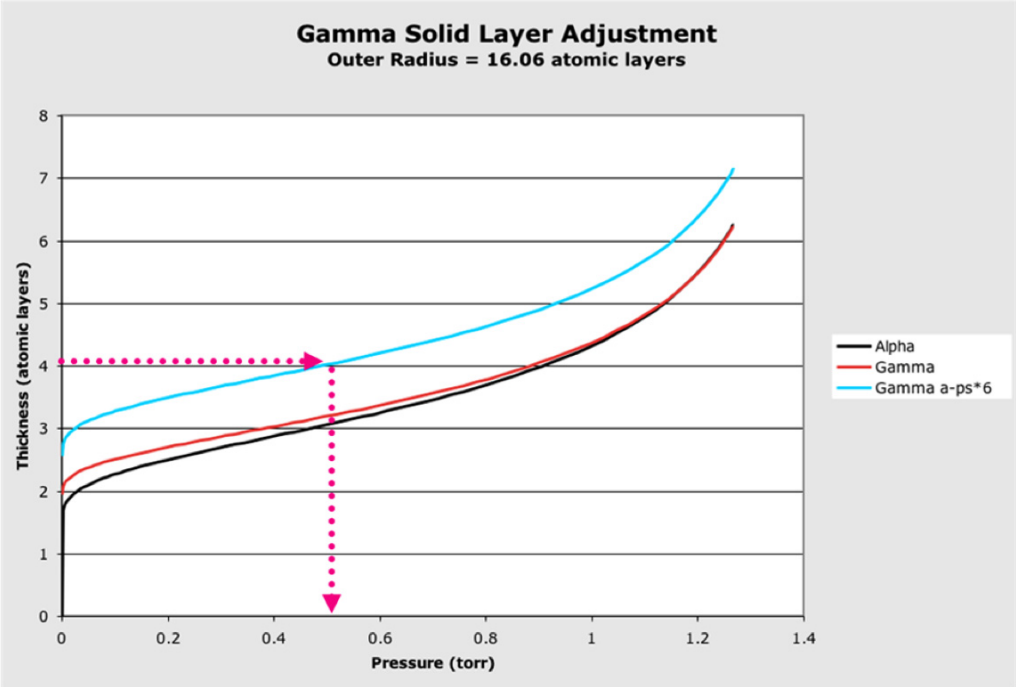

Figure 10. Chamber pressure prediction from quasi-solidification model: 4 atomic layers corresponds to ~0.5 torr

According to the nanotube filling theory, the moment of instability of the film inside of a tube signals the loss of third sound. Figure 11 shows that the corresponding pressure is about 0.1 torr.

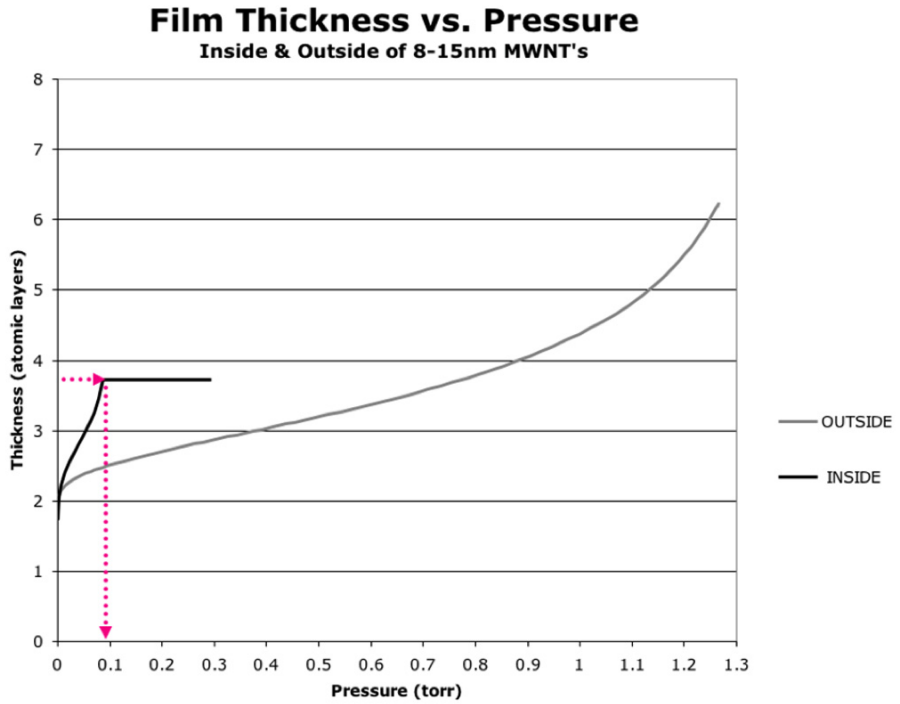

Figure 11. Chamber pressure prediction from nanotube filling model: a filled nanotube corresponds to ~0.1 torr

It turns out that the pressure associated with the loss of signal in Run 32 (Figures 1, 4, and 5) is 0.526 torr. Comparing experiment to theory, quasi-solidification is the most likely explanation for our loss in third sound signal. In addition, the nanotube filling explanation would be physically improbable: our resonant cavity is filled with a random array of nanotubes, so a coherent third sound signal propagating through the *inside* of these tubes is unlikely to exist along the entire length of the rectangle.

This conclusion is tentative, as it is only based on one experimental run. More runs need to be performed using the same setup, the same materials, and under the same conditions. Further experiments using cell materials other than plexiglass (copper, glass, etc.) will ensure that third sound isn't dependant on superfluous external conditions. If in all of these cases we still see a loss of superfluidity at about 0.5 torr, the quasi-solidification theory can be recognized as a physical explanation of superfluid behavior in thin films.

The theoretical approach could also be further adjusted. Namely, we need to apply the gamma correction to our calculation of film thickness inside of tube. To properly consider the nanotube filling hypothesis, we need a more straightforward substrate, as it is difficult to find a path within a random array of disjointed tubes. A better test of this theory would use a single nanotube, rather than a rectangle of airbrushed nanotubes. A collaboration is underway to isolate this nanotube. We are in contact with Marc Bockrath from Caltech, who has worked with doubly clamped suspended carbon nanotube nanomechanical resonators for the purpose of mass sensing. To run this experiment, we must determine how to detect third sound on such a small scale. To do so would be ideal—the results would correspond most accurately to the theories that we have developed.

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