



Aerogel: Impurities in Superfluid ^3He ?

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We present results of torsional oscillator experiments that are in progress or completed at Cornell. Taken together, these experiments suggest that the properties of superfluid ^3He in aerogel are substantially different from those exhibited by bulk superfluid ^3He . Featured are the differences between bulk and superfluid ^3He in aerogel with temperature and pressure. Comparisons to proposed models of ^3He in aerogel are also made.

1. INTRODUCTION

Twenty five years ago unconventional (p-wave triplet) superconductivity was discovered in liquid ^3He [1]. The concepts developed for the understanding of anisotropic pairing in the various superfluid phases of this quantum liquid have been adopted for the description of anisotropic superconductivity of metallic systems such as heavy fermion and oxide superconductors. Whereas the role of impurities is ubiquitous and well understood in the case of metallic superconductors, except for surfaces, they play only a minor role in the neutral superfluid ^3He . These limitations are lifted, however, with the discovery that aerogel, a collection of silica particles, can be thought of as a dilute impurity system in bulk ^3He . Aerogel has been shown to radically alter the phase diagram of mixtures of ^3He and ^4He [2]. The present work was initiated to explore the effect of aerogel on the low temperature behavior of ^3He as well as the mixtures.

This article is intended to provide a reasonably up to date summary of the experimental data obtained at Cornell on pure superfluid ^3He in 98.2% open aerogel samples. To date we have examined superflow of ^3He in three different samples of aerogel using the torsional oscillator technique. This method provides direct information on the inertia of fluid decoupled from the oscillator due to the onset of superfluidity. Despite having nominally the same open volumes, the cells show differences in their T_c vs. pressure characteristics. In the two newer cells the transition temperature is reduced from that reported by us for the original cell[3], and is comparable to that observed by the Northwestern group[4].

The paper is organized in the following manner. We first describe aerogel and what distinguishes this

material from other porous media. We then outline our results, highlighting features which we consider to be major, and others which describe important details. We then compare results to theoretical work. Finally we conclude with a summary as well as a list of some experiments which should be done and why these might be important.

2. WHAT IS AN AEROGEL?

Aerogels start as a mixture of tetra methoxysilane (TMOS) and water in a 1:4 molar ratio. The TMOS in the presence of water breaks down into $\text{Si}(\text{OH})_4$ and methanol, and the $\text{Si}(\text{OH})_4$ polymerizes into colloidal aggregates which coalesce into a gel. The final density of the gel can be changed by diluting the TMOS and water with methanol, and gels occupying less than 0.5% of the open volume can be made. The microscopic structure of the aerogel is largely set by the kinetics of the gelation process. Since the reaction rate is affected by the pH of the solution, microscopically different aerogels can be made with the same density[5]. In base catalyzed aerogels the reaction rate is accelerated, causing particles to coalesce rapidly, and aggregation is only limited by the diffusion of clusters. In neutrally reacted aerogels, the reaction rate is inhibited and aggregation is chemically limited. Since chemically limited aggregation allows diffusing clusters to make many attempts to coalesce, neutral aerogels have more evenly distributed structure over a wider range of length scales. Most aerogels are made in a base environment. After gelation, the drying process must be done hypercritically since the surface tension of a liquid-vapor interface would otherwise destroy the aerogel. The experimental cells used at Cornell were made for us by Yoon and Mulders in Moses Chan's group at Penn State.

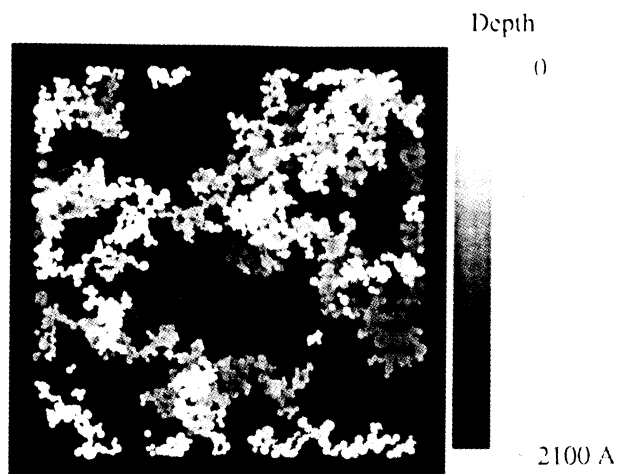


Figure 1: A computer generated image of an aerogel grown by DLCA. The constituents are 30\AA in diameter, and the cube has dimensions of 2100\AA on a side. The gray scale indicates the "depth" of the silica site from the front face.

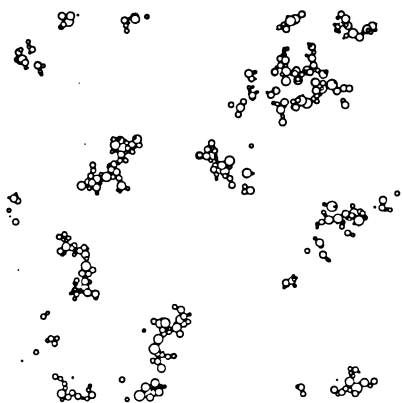


Figure 2: A 150\AA "slice" of the same cube shown in Figure 1. This image allows one to appreciate the empty volume in this structure.

In order to understand why aerogel is so different in its effect on ^3He , one must appreciate the structure of the material, beyond the low density (39.4 g/l) and large surface area ($22.9\text{ m}^2/\text{cm}^3$). It is difficult to capture the full three dimensional structure of aerogel with imaging techniques such as TEM and SEM, and X-ray scattering can only provide k-space information. Luckily, for base catalyzed aerogels, diffusion limited cluster aggregation (DLCA) is a realistic yet simple model which can provide information about the real space structure[6]. We have used the

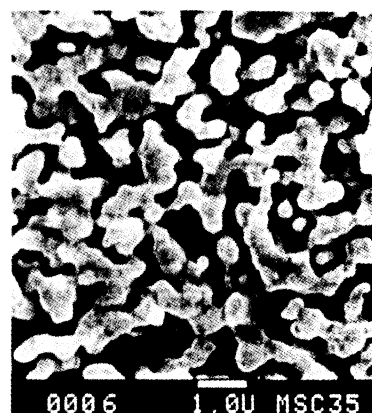


Figure 3: An electron micrograph of a 40% packed silver sinter. This image highlights the differences (pores in silver vs. open spaces in aerogel, orders of magnitude difference in silica vs. silver diameters, strands of silica vs. nearly uniform density in silver) between conventional porous media and aerogels.

DLCA model to simulate the 98.2% aerogel used in these experiments[7]. Small angle scattering calculated for the simulated aerogels is in good agreement with X-ray scattering measurements on real aerogels. In Fig. 1, we show the projection of a 2100\AA cube of computer generated aerogel. The gray scale corresponds to depth relative to the top face. The areas in black have no material that intersects the line of sight perpendicular to the top face. In Fig. 2, we show a 150\AA slice of the same cube to illustrate the clustering of the silica as well as impart an impression of the openness of the structure. The clustered particles in the model have a gaussian distribution of diameters centered on 30\AA with a spread of 15\AA . For comparison we also show (Fig. 3) a photograph of an electron micrograph of 40% (of solid density) silver sinter made from nominal 700\AA powder. The difference between the aerogel and the silver is striking. Note that the length scales of the pictures are vastly different and the smallest units in the sinter are $\sim 1000\text{\AA}$ or more in diameter, while the smallest units for aerogel are $\sim 30\text{\AA}$. This length scale in aerogel can be verified with small angle scattering[6]. For the silver, there are well defined pores that are bounded by grains of silver. In contrast, the 150\AA "slice" of aerogel reveals no pores, instead showing a very open space filling structure.

The advantage of the computer model is that it

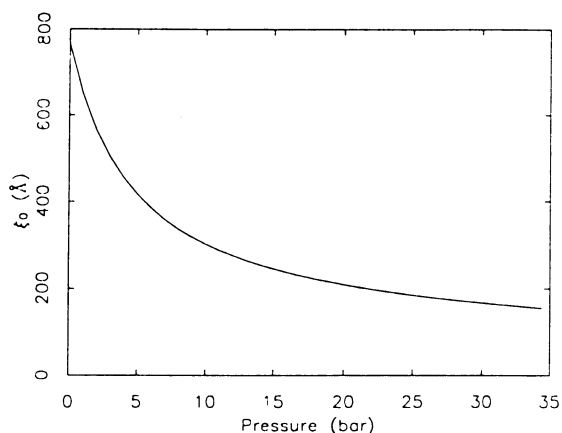


Figure 4: The zero temperature coherence length of pure ^3He , plotted vs. the pressure. Note the rapid dependence at low pressure.

is amenable to direct calculations of properties that are difficult to measure for a real aerogel. We find that the geometric mean free path scales with the volume concentration of silica, c , as $c^{-1.24}$, and for our 98.2% aerogel it is 2000\AA . For comparison, we calculated the mean free path for a 95% aerogel to be 600\AA , which is in good agreement with the experimentally observed value of 500\AA measured by Candela's group at the University of Massachusetts[8]. Of relevance to ^3He is the largest distance from any point in the open volume to a silica surface. Despite the large open volume, this distance turns out to be rather small, around 300\AA for 98.2% open aerogel. For comparison (Fig. 4), the zero temperature coherence length for bulk ^3He , $\xi_0 = \hbar v_F / 2\pi k_B T_c$ [9] ranges from 150\AA at 29 bar to 800\AA at saturated vapor pressure. The usual boundary condition of the order parameter being brought to zero within a coherence length of a diffusely scattering surface[10] would lead to a complete suppression of the superfluid at all pressures. Since the superfluid state is present in aerogel, the usual boundary condition cannot be valid at the surface of the silica.

To summarize this section, the aerogel's structure is substantially different from that of other porous media, not only because of the low density but also because the silica particle diameter is smaller than a coherence length. The small size of the smallest units (30\AA), the proximity of the entire volume to silica and the relatively long mean free path make aerogel a unique environment in which to study ^3He .

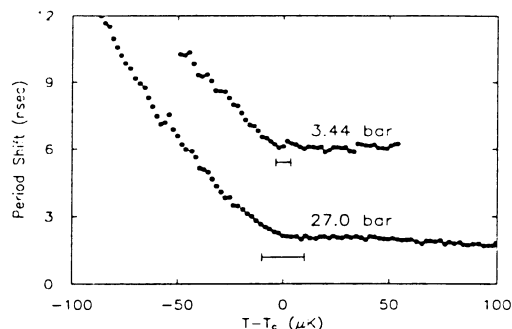


Figure 5: The period of the oscillator plotted against the temperature for two different pressures. Note the sharpness of T_c . The bars indicate 1% of the transition temperature.

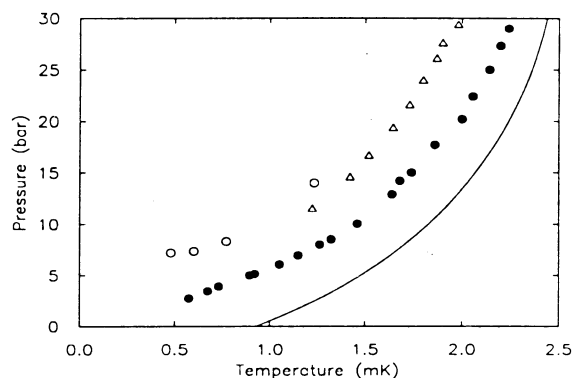


Figure 6: The phase diagram of three different aerogel- ^3He systems. While not complete, these three sets of data suggest that the overall density is but one of the factors that determines T_c .

3. ρ_s/ρ of ^3He IN 98.2% AEROGEL

3.1. MAJOR FEATURES

The first major feature is the sharpness of the transition, which we show in Fig. 5. This should be compared to the results of Freeman and Richardson[11] measured in a parallel plate geometry (at zero bar) with a size distribution of 3%. The signal is substantially sharper in the aerogel despite the broader size distribution. While such a sharp transition could be the result of a percolative behavior between regions of locally enhanced T_c , the evidence from Northwestern[4] (and most recently from Manchester[12]) indicates that the transition is global and homogeneous rather than due to the connection of individual superfluid regions.

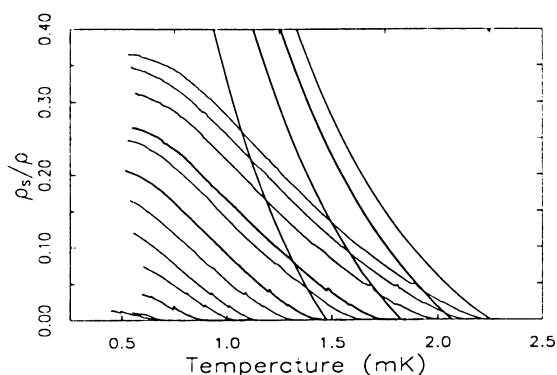


Figure 7: ρ_s/ρ for pressures between 29 and 3.5 bar (top to bottom). The bulk results at 20, 15, 10, and 5 bar (steep lines from right to left) are also shown. Note that the superfluid fraction is reduced as the pressure decreases (larger coherence lengths). Surprisingly, the curves for ^3He in aerogel nearly fall on top of one another if they are shifted in temperature.

When we first observed the superfluid transition of ^3He in aerogel at 6 bar, we were surprised that there was a superfluid phase because of the prominent role of diffuse scattering at boundaries[13, 14, 15, 16, 17]. We show in Fig. 6 the second main feature – the suppression of the superfluid transition relative to the bulk T_c , for three cells with the same (98.2%) density, but whose structural details (e.g. strand correlations) may differ slightly due to growth conditions. The density of the aerogels can be well controlled and it is unlikely that the average densities are very different. The differences in the transition temperature therefore argue for either a very strong density dependence or a strong dependence on the microscopic structure. It is also evident that there is a normal - to - superfluid transition as the density of the helium is increased at zero temperature.

The third feature is the temperature dependence of the superfluid density at different pressures. In Fig. 7, we show the development of the superfluid fraction measured for several pressures using the original cell, together with superfluid fraction in the bulk[18]. It is evident that the superfluid in the aerogel develops at a constant rate with temperature, and that this is different from the behavior of the bulk, where superfluidity develops at the same rate with T/T_c . The superfluid fraction in ^3He bulk follows a nearly pressure independent behavior if the temperature is scaled by T_c . By comparison, a plot of the development of the superfluid fraction of ^3He

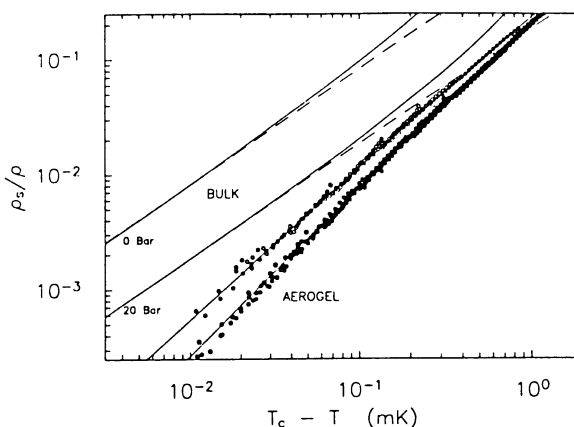


Figure 8: The power law dependence of ρ_s/ρ . The higher pressure results have a slightly larger power law. In all cases, the superfluid develops quite differently from the bulk, where the superfluid fraction is linear near T_c .

in aerogel is nearly pressure independent if the temperature is simply offset, or in other words if we plot the superfluid fraction vs. $T_c - T$ without scaling by T_c .

The fourth feature in this category is the temperature power law of the development of the superfluid. The superfluid fraction on a log-log plot (Fig. 8) displays a greater than linear power law. There appear to be two regimes. Below 15 bar (but not below 4 bar) the superfluid fraction develops with a power law of 1.3, while above 15 bar the superfluid fraction exhibits a larger (1.45) exponent. Note that all of the aerogel data lie roughly on top of each other in contrast to the bulk superfluid. This is just another way to express the third feature.

3.2. IMPORTANT DETAILS

There are other interesting features of the data which must contain important clues to the details of the pairing in superfluid ^3He in aerogel. The first is the dependence of T_c/T_{c0} with pressure. In Fig. 9, we plot ρ_s/ρ at various fractions of T_c aerogel against the pressure. Here the interesting feature is that ρ_s/ρ appears to be extinguished below ~ 3 bar. However T_c/T_{c0} is still finite at this pressure. (The apparent point at which $\rho_s/\rho = 0$ depends on the exact nature of the extrapolation.) It is evident that the behavior of ρ_s/ρ is very different from that of the bulk.

We note that pressure, though it is a conve-

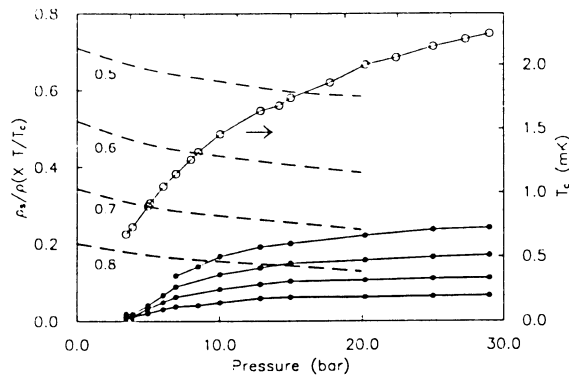


Figure 9: A plot of ρ_s/ρ (solid circles) at $T/T_c = 0.5, 0.6, 0.7, 0.8$ (solid lines from top to bottom) against the pressure. The superfluid fraction vanishes at a non zero pressure. The dashed lines indicate the pressure dependence of the bulk ρ_s/ρ at the same values of T/T_c as the aerogel data. Also shown is the pressure dependence of T_c (open circles). ρ_s/ρ and T_c appear to vanish at different pressures.

nient thermodynamic variable, is not an intrinsically useful parameter, since the compressibility of ^3He varies enormously with pressure. For example, T_{c0} changes by only 0.078 mK between 25 and 30 bar, while it changes by 0.549 mK between 0 and 5 bar. Thus, density, T_{c0} , or the zero temperature coherence length are likely better parameters for plots than the pressure.

Another feature is the low speed sound resonances that cross the resonant frequency of the oscillator in all three cells, and can be discerned in Fig. 7. Estimates of the sound speed give $c \leq 15\text{m/s}$ but a detailed analysis is complicated by possible shear modes present in the aerogel. It is likely that these resonances are similar in origin to those previously seen in experiments on He II in aerogel[19, 20]. We have observed that in our cells, these resonances are suppressed at higher amplitudes of oscillation.

To summarize this section, we have found that the transition temperature of the superfluid is strongly suppressed by the presence of aerogel. Despite having samples of the same nominal density, the transition temperature is suppressed by radically different degrees. The superfluid fraction appears to vanish in a region where the T_c appears to be finite, the power law dependence of the superfluid fraction is altered from that of the bulk.

4. COMPARISON TO THEORY

The confinement of ^3He within aerogel limits the mean free path to a constant value, orders of magnitude smaller than that of the bulk. Also, the objects that scatter the ^3He quasiparticles are of the order of 30 to 50 Å, significantly smaller than the coherence length of the superfluid ^3He . Presumably, the pressure dependence of T_c and the superfluid fraction are related to the pressure dependence of the coherence length.

In the homogeneous scattering model (hsm) developed by Thuneberg, Sauls and coworkers[21], the impurity shortens the mean free path, terms in the free energy are affected and these reduce T_c/T_{c0} as the coherence length increases (Fig. 10). However, the experiment and the hsm are in agreement only if the scattering length (a free parameter in the theory) is allowed to vary by a factor of two with pressure (Fig. 11).

Once T_c is fixed at each pressure by choosing the correct mean free path, the theory predicts the suppression of ρ_s at a particular temperature. The superfluid fraction is found to follow a dependence similar to that shown in Fig. 9, starting out a factor of two higher at high pressure but not displaying as strong a suppression as the experimental data at lower pressures. The exact dependence depends strongly on the particular texture. The strongest suppression is predicted for the A phase with $\hat{\ell} \parallel \mathbf{v}$ and the least suppression for $\hat{\ell} \perp \mathbf{v}$, with the B phase displaying an intermediate dependence.

These discrepancies between the hsm and experiment, though striking, are not unreasonable given the simplicity of the assumptions. Apparently the

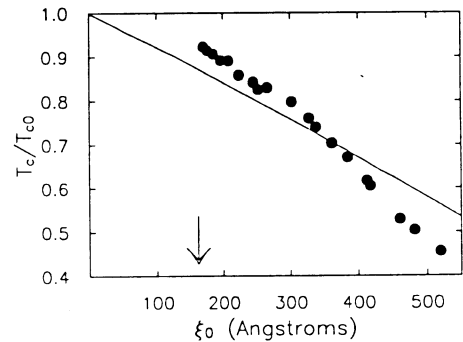


Figure 10: The suppression of T_c/T_{c0} vs. coherence length for a constant mean free path (hsm). Data from Ref. 1 shown as solid circles.

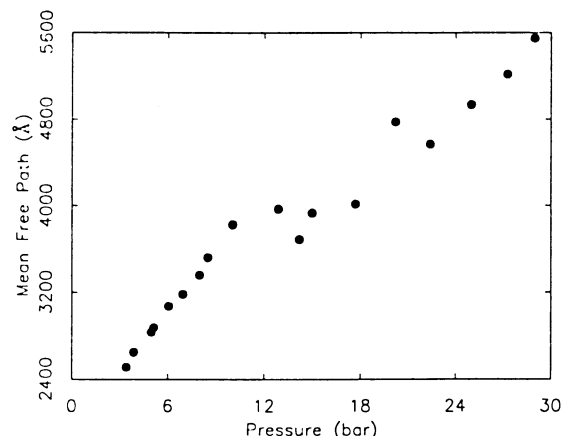


Figure 11: Calculated mean free path using Ref. 1 data and the hsm. The mean free path has to vary by ≈ 2 for a good fit.

hsm (for as yet unknown reasons) overestimates Δ^2 by a factor of 2 at high pressure and even more at low pressures. The role of inhomogeneities of the aerogel's density and the effect of these inhomogeneities on the measured quantities is still under active investigation at this time. Overall, this model does attempt to introduce real properties of aerogels and finds that there are significant consequences to the transition temperature and superfluid fraction with the introduction of impurities that limit the mean free path.

We noticed that T_c could be well approximated by the functional form $(L/\xi_0)^2 = 1/(1 - T_c/T_{c0})$, where L is a constant length ($\sim 670\text{\AA}$). This is the Ginsburg-Landau form of the temperature dependent coherence length close to T_c . It is also the functional form of the T_c suppression in a slab geometry for small T_c suppression. The full calculation of the slab model first put forward by Kjaldman et al [22] and applied to aerogel in [21] is in surprisingly good agreement with the data if the slab thickness is taken to be $\sim 1050\text{\AA}$. There is no strong reason to expect the model to work so well. The agreement of the slab model and the Ginsburg-Landau coherence length may merely signify that T_c is suppressed as a power law in ξ_0 . We plot in Fig. 12, T_c/T_{c0} against ξ_0 for the full slab model. For comparison we show the dependence of $\xi_0 = L'(1 - T_c/T_{c0})^{1/1.7}$, where L' is a fitting parameter ($L' = 730\text{\AA}$). The slab model works well predicting T_c with a single fitting length but like the hsm it cannot produce the large suppression of ρ_s at long coherence lengths.

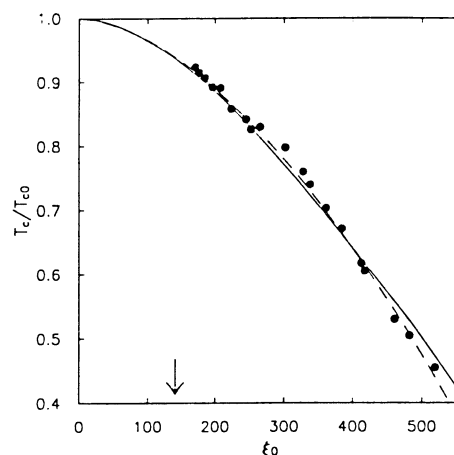


Figure 12: T_c/T_{c0} plotted against the zero temperature coherence length. The results of the slab model (solid line) as well as a power law fit of $\xi_0 = L'(1 - T_c/T_{c0})^{1/1.7}$ (dashed line) are shown.

The main strength of the slab model is to recognize that unlike the cylindrical pore model[22], the slab leads to a suppression of the order parameter primarily in one direction. It is possible that because of the inverse geometry (aerogel is not a collection of pores in solid material - it is solid in a liquid), it might make sense that the order parameter would be suppressed in only one dimension, and not two as in the cylindrical version. Clearly the slab model seems to work best at predicting T_c . Ultimately why that is so, and whether its success is a coincidence is really not clear to us. The slab model also does result in a somewhat more pressure dependent suppression of the superfluid fraction, though the experimental pressure dependence is not replicated.

The disordered order parameter model[23] is appealing, since it focuses on an obvious feature of the aerogel. The argument advanced by Volovik is that the scattering is responsible for the suppression of T_c , and that the disorder introduced by the presence of impurities disrupts the long range behavior of the order parameter and leads to a superfluid "glass". The author draws on work to model heavy fermions with impurities added[24]. A glassy order parameter can lead to a number of striking behaviors, the suppression of the frequency shift with tip angle observed in the Northwestern experiments[4], the inducing of superfluidity by the presence of a current, and the raising of T_c by the application of a magnetic field. Although the model is short on quantitative

predictions, there is some appeal to this approach, since it attempts to incorporate what would appear to be one of the distinguishing features of aerogel.

Random field arguments were also advanced by the authors of Ref.[21], who introduced these features to account for the exotic tip angle dependence observed in the Northwestern experiments[4].

In our laboratory, we have attempted to search for the effect of magnetic field and flow but have not been able to induce (or suppress) superfluidity to within our thermometers' accuracy, both by increasing the amplitude of oscillation and by the application of a magnetic field up to 1000 gauss. These measurements have not progressed to completion and so any conclusions are premature.

To summarize, the models that have been advanced are making progress towards providing a complete picture of the effect of introduction of aerogel into ^3He . However, the understanding is by no means complete, and significant discrepancies remain.

5. SUMMARY AND CONCLUSIONS

We have shown that the effect of degrees of disorder or density differences between different aerogels appears to have striking consequences on the phase diagram. Unlike bulk ^3He , the zero temperature phase diagram exhibits an entirely new qualitative feature, namely a normal to superfluid transition. T_c is sharp, ρ_s/ρ does not follow the bulk temperature dependence and scales differently with temperature. The superfluid fraction displays a strong pressure dependence and appears to be quenched at a finite T_c/T_{c0} , though the latter statement is clearly dependent on the nature of the extrapolation.

The T_c suppression, power law dependencies and the strong suppression of ρ_s are not modeled adequately by theory. This is a situation ripe for exploitation by experimentalists. Many new experiments suggest themselves. For example, the most obvious one, an examination of the superfluid density and NMR in a single cell is underway at Manchester and appears to indicate that the T_c is identical, which is good news indeed[12]. At Cornell, we have started a number of experiments to measure ρ_s in a magnetic field and with ^4He added. These indicate that there isn't a double superfluid (at least as far as we can see). In collaboration with Chan at Penn State and Mulders, we will be looking at ρ_s in a variety of different density samples. This will hopefully tell us the dependence of T_c and ρ_s on density, and should reveal how the phase diagram of ^3He in aerogel eventually joins up to the bulk phase diagram.

Specific heat would tell us the order of the transition and possibly reveal the topology of the gap's node structure. Sound measurements show promise for the future detection of ^4He and ^3He superfluids that may be present simultaneously. Ultrasound spectroscopy is a natural technique to measure the magnitude and temperature dependence of the gap as well as the collective mode structure. Flow experiments in a magnetic field are needed to establish the validity of the glassy order parameter model. Additionally, measurements need to be done in the normal fluid to determine the spin diffusion length or mean free paths.

In conclusion, ^3He in aerogel allows the exploration of a significantly different parameter space from that of bulk ^3He . We can add impurities at different densities, controlled amounts of disorder and understand the new effects on the only well understood exotically paired superfluid. There seem to be a number of opportunities to pursue and understand this spectacular and interesting model system.

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