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Bulk-like Excitations in Nanoconfined Liquid Helium

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The effects of confinement, disorder, and reduced dimensionality upon quantum fluids have been studied by the adsorption of liquid helium in porous media. The effects of extreme, nanoscale confinement upon its microscopic excitations are not presently understood. Several previous experiments have suggested that, at sufficiently low temperature, the roton mean free path is set by the restricted geometry. Here we show that the lifetime of the roton excitation is unaffected when superfluid helium is confined within cylindrical pores only a few nanometers in diameter. The temperature-dependence of its lifetime are found to be identical to the bulk fluid, implying that the lifetime is not set by the scale of the confinement. Our results demonstrate that the rotons in the pore center propagate without being modified by the confining media, unlike the collective excitations of classical fluids.

I. INTRODUCTION

Liquid helium confined in porous media provides a model system for the study of the effects of confinement, quenched disorder, and reduced dimensionality on strongly interacting Bose fluids[1–8]. Studies of the effects of confinement on the elementary quasiparticle excitations has been particularly illuminating. In the bulk liquid the excitation spectrum exhibits a single branch - the phonon-roton spectrum - whose most prominent feature is a sharp dip at finite wavevector Q known as the roton. Macroscopic properties, such as the superfluid fraction[9], are primarily determined by the roton and measurements of the roton temperature dependence accurately predict these properties over a large range of temperatures. Under confinement the excitation spectrum develops two distinct branches: a bulk-like phonon-roton spectrum associated with liquid in the center of the pore and a new branch due to a compressed layer of liquid at the pore surface. This behavior has been observed in a wide variety of confining media and has been shown, in Vycor, to explain the observed behavior of the heat capacity and superfluid fraction[10–13].

The effects of confinement on the roton remain an open question in contrast to the bulk where the behavior is quite well understood. The bulk liquid roton has a well defined energy and infinite lifetime (i.e. zero linewidth) at T=0 K and, with increasing temperature, the energy softens and the linewidth increases[14–17]. In addition, the energy and lifetime exhibit the same temperature dependence indicating a common origin. Bedell, Pines, and Zawadowski (BPZ)[18] accurately described this behavior by considering four roton scattering processes and predicted that both the softening and broadening of the roton were proportional to the thermal population of rotons. In large pores the energy and lifetime of the roton appears similar to the bulk liquid. Striking differences arise in small (<5 nm) pores[10,19–21].

The roton linewidth mirrors the bulk behavior at high temperatures, when the bulk mean free path is short, and approaches a finite non-zero value at low temperatures, where the bulk mean free path would be larger than the pore size. In contrast, even in extreme confinement the energy of the roton remains identical to the bulk indicating that the direct connection between the energy, lifetime and mean free path that exists in the bulk breaks down.

However, it remains a mystery as to why scattering due to the confining environment would affect the lifetime but not the energy. In this paper we present a high-resolution neutron scattering investigation of the collective excitations in small pores that directly addresses this open question. We find that, in extreme confinement, both the roton energy and lifetime have a temperature dependence that is identical to the bulk. At the same time, the roton excitation in the compressed layer is much broader than the bulk and nearly temperature independent. This suggests that the confined fluid is effectively decoupled from the dense interfacial layer and the pore walls. Since the mean free path of the roton is much larger than the pore size at low temperatures this implies that rotons scatter elastically from the dense liquid layer and that their lifetime is not limited by interactions with the pore walls.

Upon adsorption in small pores helium first forms a solid layer(s) at the pore wall[19,20,22–24]. This is followed by the formation of a liquid layer on top of the solid layer with a density that is higher than the bulk liquid. This dense liquid layer has a roton-like excitation (i.e. it exhibits a dispersion with a minimum at a finite momentum transfer Q) but with an energy and momentum that is different from the bulk roton. In Vycor this layer mode dispersion was used with a two-dimensional density of states to reproduce the heat capacity[10]. In addition, this excitation in the dense liquid layer is quite broad (≈400 μeV)[19] and both the energy and lifetime are practically temperature independent.

Adsorption of additional helium into the pores results in the formation of a bulk like liquid in the pore center. This bulk like liquid exhibits an excitation spectrum identical to the bulk liquid with a phonon branch at low momentum transfer Q ($Q < 0.7$ Å^{-1}) and a roton minimum at higher Q (1.9 Å^{-1}). The velocity of sound for the phonon and the excitation energy and Q for the roton as a function of temperature are identical, to within experimental errors, with the bulk. Furthermore, in larger confining geometries (> 5 nm) the width of the roton excitation as a function of temperature is also identical to the bulk[11 25]. In smaller pores, however, the linewidth has been reported to approach a finite value at low temperatures[10,19–21].

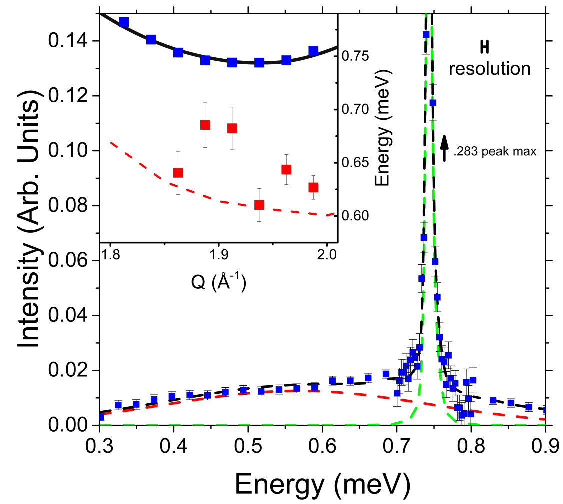

FIG. 1. A cut of the dynamic structure factor S(Q,E) along the roton minimum Q_R at 0.34 K. The inset shows the dispersion, for both the bulk-like mode and the layer mode. The low intensity layer mode is plotted with wide bins to increase statistics, while the strongly scattering bulk-like mode is plotted with narrow bins to resolve the width. The total fit (black dotted line) is comprised of a linear background, a Gaussian layer mode (red dotted line), and a Damped Harmonic Oscillator bulk-like mode (green dotted line). Error bars throughout the text represent one standard deviation, derived from the square root of detector counts and binned using standard data reduction software[30,31].

II. EXPERIMENTAL APPROACH

To resolve this discrepancy we have carried out inelastic neutron scattering in a ordered porous material with small pores. FSM-16[26] is a mesoporous silica consisting of monodisperse cylindrical pores of 2.8 nm diameter and large (100s of nm) lengths arranged in a triangular lattice. Adsorption and thermodynamic properties of helium thin films in this material have been measured extensively[5,7,19,27,28]. FSM-16 was synthesized using methods described in detail elsewhere[26]. The material was characterized using X-ray diffraction and N_2 adsorption isotherms yielding a Brunauer-Emmett-Teller (BET) surface area of 1014 m^2/g and a pore size distribution is peaked near 28 Å with a full-width half-max of ≈2 Å. ^{4}He adsorption isotherms yielded a full pore helium adsorption of approximately 47 mmol/g.

The neutron scattering measurements were carried out using the Backscattering Silicon Spectrometer (BASIS)[29] at the Spallation Neutron Source. BASIS is a time-of-flight backscattering spectrometer with silicon crystal analyzers providing high-resolution (≈3.5 μeV) over a wider dynamic range (300 μeV < E < 1000 μeV) at momentum transfers of 1.0 Å^{-1} < Q < 2.0 Å^{-1} using the Si(111) analyzers. An aluminum sample cell with neodymium magnets was attached to an Oxford HelioxVT insert with a sample fill line to allow volumetric loading of ^{4}He gas into the sample cell. Measurements were carried out with gas loadings of 0 mmol/g and 43.0 mmol/g. The scattering from bulk liquid helium at low temperatures was used as an experimental measurement of the instrumental resolution.

The unintended condensation of bulk liquid helium within the neutron beam is a potential source of error that we have been careful to avoid. The background scattering from the empty porous material and cryostat did not produce a visable roton signal. While loading gas to the sample, the pressure of the cell was kept lower than the bulk liquid vapor pressure to avoid condensing bulk liquid within the cell. During a typical run, the temperature gradient between the ^{3}He still and the sample cell was approximately 35 mK. The contribution of helium outside the pore space to the scattering is small, as the external surface area of the FSM-16 powder is approximately 1% of the total surface area[27].

III. RESULTS

The scattering from confined liquid helium was measured as a function of temperature at full pore filling from

0.34 K to 1.50 K. The observed scattering at 0.34 K at the roton minima (Q=1.94 Å^{-1} bin) is shown in Fig. 1 and consists of two components. The first is a resolution-limited excitation at 0.74 meV consistent with the bulk roton. This excitation exhibits a pronounced temperature dependence both in its energy and lifetime reflected in the peak center and peak width. The second is a broad excitation that has been associated with the dense liquid layer at the pore walls[32] and is essentially temperature independent both in terms of its energy and lifetime.

The roton is characterized, to first approximation, by the Landau equation E = $\Delta + \hbar^2(Q - Q_R)^2/2\mu$ with a minimum Q = Q_R, energy gap Δ, and effective mass μ. To extract these parameters we fit the dynamic structure factor S(Q,E) to a Damped Harmonic Oscillator function convoluted with the measured experimental resolution. Except at the lowest temperatures the resolution was a minor contribution to the observed width. At the lowest temperatures studied the scattering of the narrow bulk-like roton line was essentially resolution limited. The extracted values of Δ are identical, to within experimental errors, to the bulk values at all temperatures studied. The values of Q_R and μ are also identical to bulk values of 1.925 Å^{-1} and 0.136 to 0.153 ^{4}He mass[15] and temperature independent.

The softening of the roton mode in both the bulk and several small pore porous media is shown in Fig. 2. We note that we have shown the shift in the roton energy gap Δ(0) - Δ(T), to highlight the similarities to the lifetime, and that we have used the lowest temperature measurement in each system as an estimate of Δ(0). As can be seen, the observed energy gaps in the bulk fluid and the liquid confined in pores 3 to 7 nm in size are identical to within experimental error. In addition, both the bulk and our confined measurements are well described by the BPZ theory using the bulk value for the roton-roton scattering cross section.

Intrinsic (resolution corrected) roton linewidths from both bulk and confined helium are shown in Fig. 3. Both our measurements and previous studies are in reasonable agreement with the bulk liquid at temperatures above 1.2 K. In addition, these measurements are in reasonable agreement with the BPZ predictions at these high temperatures. At temperatures below 1.2 K the previous studies have reported a finite and nearly temperature independent linewidth. This implies a finite lifetime for the roton which is not determined by roton-roton scattering as in the BPZ theory and has been attributed to scattering of the rotons by the confining geometry.

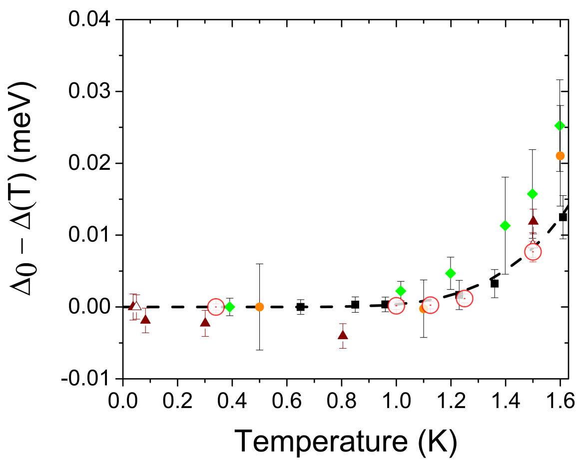

FIG. 2. Measured values of the shift in the energy gap from base value as a function of temperature, $\Delta_0 - \Delta(T)$. BPZ theory, dashed line; FSM-16 current measurement, red circles; FSM-16 43.0 mmol/g CNCS, maroon triangles[19]; FSM-16 46.4 mmol/g CNCS, open maroon triangles[19]; Vycor, orange circles[10]; MCM-41, green diamonds[20]; Bulk liquid, black squares[15].

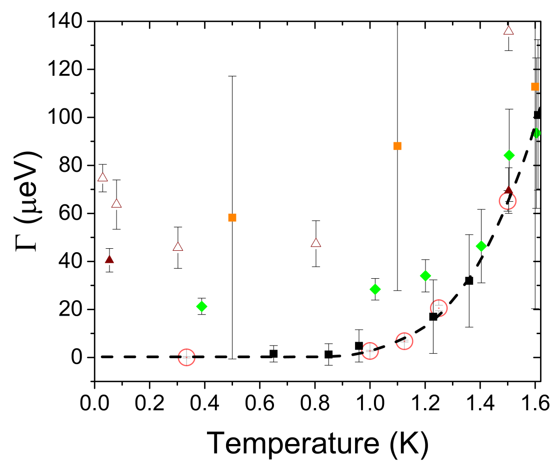

FIG. 3. Reported linewidths (full width-half max) for ^{4}He confined in porous media as a function of temperature. Points used here are identical to the ones used in Fig. 2.

IV. DISCUSSION

Our measurements differ markedly from previous studies of the linewidth at low temperatures. We find that the intrinsic linewidth approaches zero at low temperature and does not exhibit the finite values observed in previous studies. Furthermore, we note that, like the roton energy, our measurements are in good agreement with both the bulk values and the BPZ predictions throughout the entire temperature range. We do note that our measurements were carried out with very high energy resolution that was an order of magnitude better than in previous studies. Thus, in our measurements instrumental resolution is a negligible correction to the measured linewidths except at the very lowest temperatures. Furthermore, the inelastic energy resolution function was determined by measuring the bulk liquid excitations under the same experimental conditions as the confined fluid and does not rest upon any analytic approximations[4].

The exact correspondence of the energy and lifetime of the roton in the bulk and confined liquid indicates that they are governed by the same physical process - roton-roton scattering - in both cases. Within the BPZ theory, which provides an excellent description of the temperature dependence in both the bulk and confined liquids, both the lifetime and energy are proportional to the mean free path of the roton.

The roton-roton scattering cross section[33] of ≈0.07 nm^2 is temperature independent and it is reasonable to assume that it is the same in the confined fluid. Thus, the mean free path is determined by the number of thermally generated rotons[34] which is proportional to $\sqrt{T}e^{-\Delta/k_B T}$. The mean free path is 460 nm at 1.5 K and increases with lower temperature to 3.2E+11 nm at 0.34 K. The roton number density decreases with temperature as there are fewer thermally activated rotons at lower temperature, leading to a longer mean free path between roton-roton collisions.

The long mean free path at low temperatures for the confined liquid seems inconsistent with confinement in small pores. The mean free path at 0.34 K, the lowest temperature we studied, due to roton-roton scattering is macroscopic in length scale(3.2E+11 nm). This is far larger than the 2.8 nm pore diameter and one would expect that roton-pore scattering would dominate at low temperature leading to temperature independent values for both the roton energy and lifetime.

Previous studies, at lower resolution, have suggested that the roton does indeed have a lifetime that is determined by the pore size at low temperatures. This behavior has also been observed in semi-classical liquids. The collective excitations in confined D_2[35] strongly couple to the pore walls, leading to a frictional effect that reduces molecular diffusive mobility and shortens the lifetime of the collective modes. The rotational and translational dynamics of H_2 are also damped by confinement[36] due to the pore walls. Previous studies of liquid helium also deviated from bulk-like behavior, with several studies reporting linewidths larger than the bulk liquid[10,19–21] in small pores.

Our measurements clearly demonstrate this is not the case. The bulk-like roton obeys the BPZ theory with the same parameterization as the bulk liquid. This suggests that no new decay mechanisms are available and that the effective roton-roton potential is unchanged in confinement. In sharp contrast to the collective excitations of classical liquids, neither the presence of the interface nor the restricted geometry affects the energy and lifetime of the bulk-like roton. A recent neutron scattering study of liquid helium confined in MCM-41, a similar porous material, found that the bulk-like roton does not spontaneously decay into two layer modes[37]. Our findings generalize this result, excluding other conceivable decay mechanisms, such inelastic scattering between layer modes and bulk-like rotons.

We propose that the dense liquid layer that exists between the adsorbed helium on the surface of the pore and the bulk-like liquid in the center of the pore acts as a barrier layer that elastically scatters rotons in the bulk-like liquid. Several studies have examined this dense liquid layer and they have all observed that it exhibits a roton-like excitation but with an energy, effective mass, and momentum that are significantly different from the bulk liquid. Computational studies have also suggested that this dense liquid layer does not make atomic exchanges with the core liquid[22]. We suspect the difference in energy between the bulk-like rotons in the pore center and the rotons in the dense liquid layer mode prevents them from satisfying conservation of energy and momentum in roton-roton collisions. Similar kinematic contraints on phonons propagating from the bulk liquid into solid media play a role in Kapitza resistance[38,39]

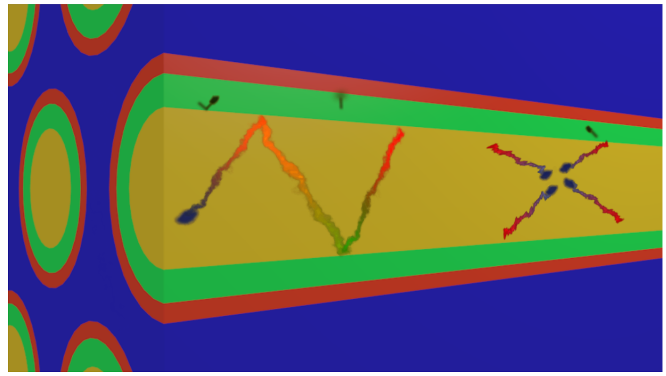

FIG. 4. A schematic depiction of rotons confined in FSM-16. The silica walls are shown in blue, while the solid, dense liquid layer, and bulk-like helium layers are drawn as red, green, and yellow respectively. The rotons are depicted as moving ballistically through the pore space, undergoing elastic collisions with the dense liquid layer. Four roton processes that are responsible for limiting the excitation lifetime are also shown.

The process we propose is shown schematically in Fig. 4. Similar to the behavior of photons in fiber optic cables the rotons in the bulk-like liquid in the pore center scatter elastically at the interface with the dense liquid layer. They can undergo many collisions as they proceed along the one dimensional pore. It is only when they interact with other rotons, and not the interface, that they can undergo collisions that change their energy and lifetime. Likewise, the rotons in the dense liquid layer mode do not exchange energy or momentum with the bulk-like rotons in the center of the pore. However, they can interact with the solid layer adsorbed at the pore surface. Due to the much richer range of excitations that exists in this solid layer they are able to exchange energy and momentum which, along with a non-bulk density, results in their significant shift in energy and their finite temperature independent linewidth.

V. CONCLUSIONS

In conclusion our studies have shown that, even in extreme confinement, the energy and lifetime of the rotons in the liquid at the center of the pore have the same magnitude and temperature dependence as the bulk liquid. We have proposed that the rotons in the bulk-like liquid are isolated from the effect of the confining media by the dense liquid layer that occurs between the liquid in the center of the pore and the adsorbed helium layer on the pore surface. Thus, rotons in the bulk-like liquid cannot exchange energy with the dense liquid layer. Instead they scatter elastically from the interface and can propagate along the pore axis.

VI. ACKNOWLEDGEMENTS

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