Anomalous Suppression of Superfluidity in ^{4}He Confined in a Nanoporous Glass

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We explore the superfluidity of ^{4}He confined in a porous glass, which has nanopores of 2.5 nm in diameter, at pressures up to 5 MPa. With increasing pressure, the superfluidity is drastically suppressed, and the superfluid transition temperature approaches 0 K at some critical pressure, $P_c \sim 3.4$ MPa. The feature suggests that the extreme confinement of ^{4}He into the nanopores induces a quantum phase transition from a superfluid to a nonsuperfluid at 0 K and at P_c.

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^{4}He confined or adsorbed in porous media provides us an excellent example of an interacting Bose system. The system dimensionality and interatomic interaction can easily be controlled by changing pore size, pore structure, and ^{4}He density [1–3]. In addition, disorder in the porous structures results in remarkable effects on the properties such as the superfluid critical phenomena [4]. The recent discovery of a possible supersolid state of ^{4}He in a porous Vycor glass draws renewed interest to this system [5].

In the case of ^{4}He confined in 10-nm narrow pores, the pressure-temperature ($P - T$) phase diagram is altered; i.e., freezing is inhibited and the superfluidity is slightly suppressed. For ^{4}He in a Vycor glass, which has randomly and three-dimensionally (3D) connected pores of 6-nm diameter, the freezing pressure below 1.5 K increases to 4 MPa and the superfluid λ line shifts approximately 0.2 K from that of bulk ^{4}He [Fig. 3(a)] [6–9]. These behaviors are attributed to the inhibition of crystal nucleation in narrow pores and the suppression of the superfluid order parameter near the pore walls.

As the suppression of superfluidity is enhanced with decreasing pore size [8], an interesting question arises: If the pore size drastically decreases and approaches the superfluid coherence length, how is the superfluidity suppressed? In this Letter, we demonstrate that the confinement of ^{4}He in a nanoporous medium leads to a strong suppression of the superfluidity, resulting in a radical change in the phase diagram.

We study the pressure effects on the superfluid ^{4}He confined in a porous Gelsil glass [10], whose structure is characterized by a 3D random network of nanopores, similarly to Vycor. The present Gelsil sample, however, has significantly smaller pores of 2.5 nm nominal diameter. The superfluidity of the adsorbed ^{4}He films in a similar Gelsil sample was studied by Miyamoto and Takano [11]. T_c for ^{4}He filled in the glass was found to be 0.9 K. This suppression of T_c at saturated vapor pressure suggests a further suppression at higher pressures.

Our Gelsil sample is a disk of 5.5 mm diameter, with a thickness of 2.5 mm, and a weight of 55.25 mg. We heated the glass up to 150 °C in vacuum to remove adsorbed water from the pores. The surface area obtained by N_2 adsorption measurement at 77 K is 26.9 m^2. We measured the superfluid response with a torsional oscillator. It consisted of a brass cell containing the glass disk, and a Be-Cu hollow torsion rod, which acts as a ^{4}He filling line. In order to uniformly pressurize ^{4}He in Gelsil, we locate a 0.5-mm thick interspace between the glass and the filling line (Fig. 2). The cell oscillates at a frequency $f \sim 1956.45$ Hz, with a high Q, e.g., $Q \sim 4 \times 10^6$ at 10 mK. It is cooled to 9 mK with a dilution refrigerator.

We measure the temperature dependence of the frequency shift from the "background" frequency of the empty cell, $\Delta f(T)$, which is proportional to the superfluid density; $\rho_s(T)$, in a very wide range of ^{4}He density. We feed ^{4}He into the cell and control the density using a room-temperature gas handling system (GHS). When the fed ^{4}He does not fill the pores, it forms a thin film on the pore walls, referred to as the film state. When ^{4}He is continuously fed, the liquid ^{4}He fills the pores, the cell interspace, and the filling line. We can then control and monitor the pressure in the cell, P, using GHS. This state is denoted as the pressurized state.

At $T < 1$ K and above the bulk freezing pressure $P_f = 2.53$ MPa, the bulk ^{4}He in the interspace of the cell solidifies. The cell pressure cannot be measured at room temperature because the filling tube is blocked by solid ^{4}He. We make the bulk solid ^{4}He in the interspace by capillary blocking technique [6,7]. We start at the "initial" pressure $P_{\rm ini} > 4$ MPa at $T > 2.5$ K, and then slowly cool the system through liquid-solid coexistence.

We observe distinct superfluid transitions in both the film and the pressurized states. In the film states, we show $\Delta f(T)$ in Fig. 1(a), and the dependence of T_c on coverage n in Fig. 3(b). Up to a critical coverage $n_c = 20\ \mu$mol/m^2, no superfluidity is observed due to the strong van der Waals attraction from the glass wall. As n increases, the superfluid film grows on the nonsuperfluid layers, and T_c increases almost linearly. These features are common in ^{4}He films adsorbed on various porous substrates, and are possibly a manifestation of interesting natures in both 2D and 3D superfluidity [1,2].

At $n = 33\mu$mol/m^2, T_c reaches a maximum, 1.43 K. Above this coverage, we observe in $f(T)$ a contribution

from the bulk ^{4}He accumulated in the cell interspace; i.e., the liquid ^{4}He fills the pores. Subsequently, T_c slightly decreases to 1.35 K. The maximum T_c we observed is 1.6 times higher than that observed by Miyamoto and Takano [11]. Moreover, there are substantial differences in the $\Delta f(T)$ curves. The average pore size in the sample we used may be slightly larger than that used by them.

We achieve the pressurized states as more ^{4}He is added. The pressure in the pores is then controlled at room-temperature. The presence of the bulk liquid in the cell, however, causes an uncertainty in $\Delta f(T)$. Hence, Fig. 1(b) shows $f(T)$ for various pressures, by shifting the ordinates in order for the data for temperatures above T_c collapse onto a single curve. The frequency varies abruptly at approximately 2 K because of the λ transition of the bulk ^{4}He in the cell.

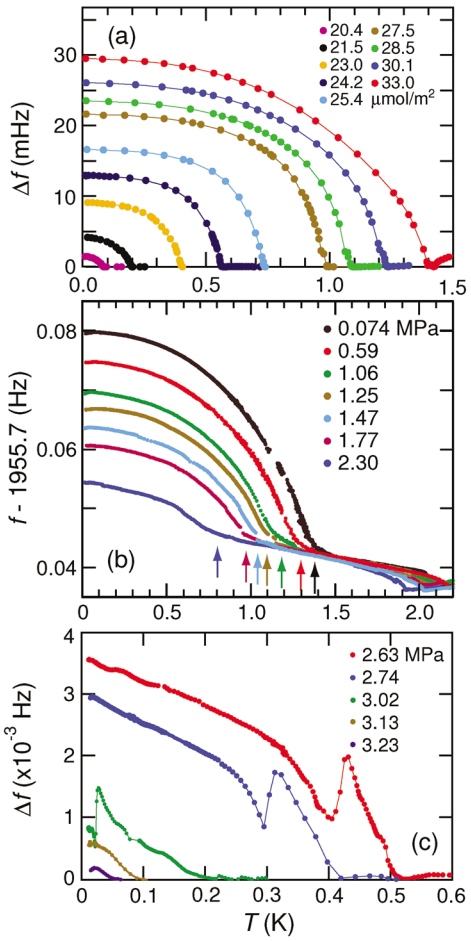

FIG. 1 (color). (a) $\Delta f(T)$ in the film states for various coverages, from $n = 20.4$ to 33.0 μmol/m^2. (b) $f(T)$ in the pressurized states. To clarify the superfluid transitions, the frequencies are shifted so as to collapse onto a single curve between one and 1.5 K. The ordinate is valid for the data of 0.074 MPa. Arrows indicate T_c's. (c) $\Delta f(T)$ for various pressures above P_f. The "n-shape" anomalies are caused by resonant couplings to superfluid fourth sound.

T_c and Δf decrease monotonically with increasing P. We plot T_c in the phase diagram shown in Fig. 3(a). At P_f, T_c reaches 680 mK, i.e., half of T_c at 0 MPa.

We measured at higher pressures, after making solid ^{4}He in the interspace by capillary blocking. When solid ^{4}He is formed in the interspace in a cooling process, we observed a large frequency drop of approximately 0.6 Hz in a narrow temperature range that depends on the initial pressure. After the complete solidification, $f(T)$ becomes similar to that of the empty cell. In the inset of Fig. 2, we show $f(T)$ for such situations. We clearly observed the superfluid transitions, which indicated that ^{4}He in the Gelsil sample remains liquid.

We estimate P in the cell by calculating $f(P)$ for the above situations, and comparing it with the data. The frequency is given by

$$f(P,T) = \frac{1}{2\pi}\sqrt{\frac{\kappa(T)}{I_c + I_{pl}(P,T) + I_s(P,T)}}, \qquad (1)$$

where $\kappa(T)$ is the torsion constant of the rod, and I_c, $I_{pl}(P,T)$, and $I_s(P,T)$ are the rotational moments of inertia of the empty cell, the liquid in the pores, and the bulk solid in the interspace, respectively. I_c and $\kappa(T)$ are derived from the $f(n)$ data in the nonsuperfluid films.

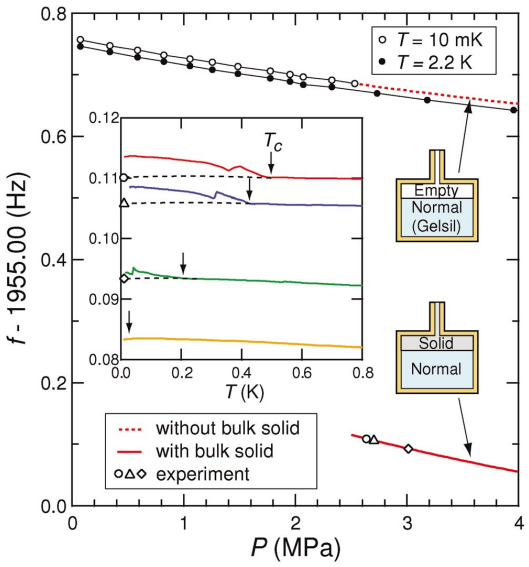

FIG. 2 (color). Estimation of the cell pressure above P_f. Solid circles: f at 2.2 K. Open circles: extrapolation of $f(T > T_c)$ to 10 mK. Assuming a parallelism at $P > P_f$, $f(P)$ is obtained as the dashed line. Here, ^{4}He is an imaginarily normal liquid in the pores, while the interspace is empty, as shown in the upper cross-sectional illustration. Adding the contribution of the bulk solid (the lower illustration), the $f(P)$ for the background frequency at ten mK is obtained as the red line. The inset shows $f(T)$ for various $P_{\rm ini}$'s. Arrows: T_c. Dashed curves: the empty-cell backgrounds. Colored circles in the main panel and inset show the corresponding frequencies.

We first determined $I_{pl}(P)$. In Fig. 2, we plotted $f(P)$ measured at 2.2 K. In this case, ^{4}He is a nonsuperfluid liquid in both the pores and the interspace, and P in the cell is equal to $P_{\rm ini}$. As P rises, f decreases because of the increase in ^{4}He density. At 2.2 K, the bulk normal ^{4}He in the interspace contributes to f, rendering the analysis difficult; whereas at the lowest temperature, 10 mK, the bulk contribution dies. Hence, we can evaluate $I_{\rm pl}(P)$ from $f(P)$ in which the liquid inside the pores is *imaginarily normal*, while the bulk part is a perfect *superfluid*. We estimate $f(P)$ by extrapolating $f(T)$ at $T > T_c$ [Fig. 1(b)] down to 10 mK, assuming the temperature dependence of the empty cell. The results are depicted as open circles. As the $f(10\ {\rm mK})$ line is clearly parallel to $f(2.2\ {\rm K})$, it is reasonable to presuppose that the parallelism holds at $P > P_f$. We estimate $f(P, 10\ {\rm mK})$ at $P > P_f$ by shifting $f(P, 2.2\ {\rm K})$. The red-dashed line indicates $f(P) = \sqrt{\kappa(T)/[I_c + I_{pl}(P)]}/2\pi$.

We then calculate $I_s(P)$ from the dimensions of the interspace and the pressure dependence of the molar volume of the solid ^{4}He at 0 K [12]. Including $I_s(P)$, $f(P)$ (Eq. (1)) is evaluated as the red solid line. This $f(P)$ curve corresponds exactly to the change in the 10-mK background frequency, which is seen in the inset of Fig. 2. We eventually determine P for each data set by comparing the background frequency at 10 mK with $f(P)$. The comparison results are represented as colored circles.

In Fig. 1(c), we show $\Delta f(T)$ for $P > P_f$. As P increases, both T_c and Δf decrease monotonically. We find that $T_c = 38$ mK at $P = 3.33$ MPa. This is the lowest T_c observed so far. At $3.6 < P < 5.0$ MPa no superfluidity is detected.

All the T_c data are plotted in the phase diagram in Fig. 3. We find that T_c approaches 0 K at a *critical pressure* $P_c \sim 3.4$ MPa. This feature radically differs from that in bulk ^{4}He or ^{4}He in Vycor, in which the "T_c line" terminates at the freezing curve.

By extrapolating $f(T)$ and the background data to 0 K, we obtain $\Delta f(0)$, which is proportional to $\rho_s(0)$. This is shown in Fig. 4 as a function of pressure. As well as T_c, $\Delta f(0)$ decreases continuously to zero. Note that $\Delta f(0)$ is downward convex, while T_c is upward convex. The error bars below P_f are caused by an uncertainty in the extrapolation.

The continuous suppression of T_c and $\rho_s(0)$ to zero are quite unprecedented for ^{4}He in other restricted geometries [6–9], in which the changes in the phase diagram were merely quantitative; the T_c line slightly shifts in parallel with the bulk λ line. The superfluid suppression in Gelsil cannot be attributed to the ordinary superfluid size effect. Moreover, contrary to the bulk superfluid-solid transition, which is a first-order phase transition, the present transition at 0 K is *continuous*.

The decrease in $\rho_s(0)$ with increasing P was also observed in ^{4}He in Vycor, and was attributed to the blockade of pores by solid ^{4}He [8]. If ^{4}He locally solidified in some pores, the superflow would be blocked, resulting in a decrease in $\Delta f(T)$. However, T_c would not decrease, because such solid plugs do not affect genuine superfluid density. Therefore, the suppressions in both T_c and $\rho_s(0)$ observed in the Gelsil sample are not due to the classical blockade, rather due to the essential change in the nature of superfluidity. This conclusion is supported

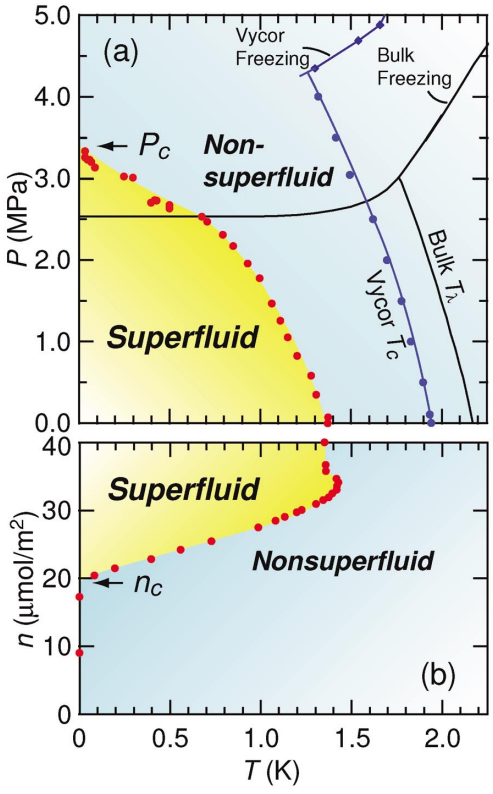

FIG. 3 (color). (a) P-T phase diagram. The yellow area shows the superfluid phase in Gelsil. Phase boundaries of bulk ^{4}He and ^{4}He in a porous Vycor glass [8] are also shown. (b) Phase diagram for the film states.

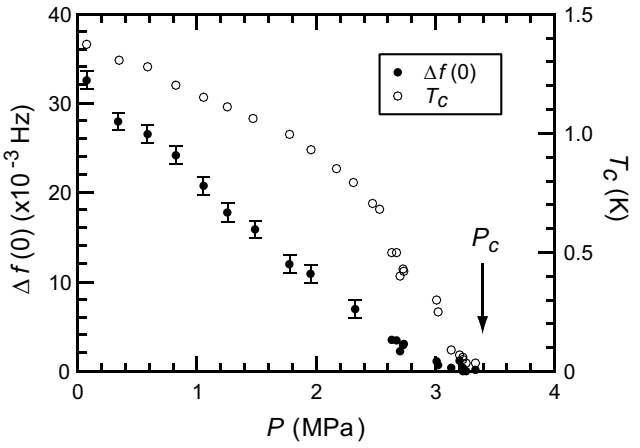

FIG. 4. Estimated Δf at 0 K and T_c as a function of P.

by the observation of fourth-sound resonances, which are seen as "n-shape" anomalies in $\Delta f(T)$ of Fig. 1(c). The existence of fourth sound ensures that superfluidity takes place at a macroscopic scale.

As shown in Fig. 4, T_c and $\Delta f(0)$ above P_f are smoothly connected to those below P_f. This ensures that the pressure estimation above P_f is reliable. However, there might be sources of systematic error [13]: (1) The assumption of the parallelism in the $f(P)$ curves at 2.2 K and 10 mK; (2) Frost heaving might produce pressure differences of the order of 0.1 MPa between the liquid in the pores and the bulk solid [14]. However, these errors can merely change the *pressure scale*. Even if such errors existed, we can evidently conclude the existence of P_c, above which ^{4}He no longer supports superfluid.

All the above mentioned results suggest that ^{4}He confined in the nanopores of the Gelsil sample undergoes a continuous quantum phase transition (QPT) at P_c and at 0 K, in the sense that the continuous superfluid-nonsuperfluid transition is driven at 0 K by changing pressure as an externally controllable parameter [15]. For further confirmation of the QPT, the nature of the nonsuperfluid state near P_c needs to be elucidated. We have found no indications of solidification up to 5 MPa; Torsional oscillator may not detect solidification in the pores. Bittner and Adams measured the ^{4}He freezing curve in an other porous glass of 2.4-nm pore size down to 1.4 K. It was nearly the same as that in Vycor [9]. Even if we assume that our ^{4}He-Gelsil system has a similar freezing curve, it is difficult to predict its behavior below 1 K. We currently are preparing a simultaneous measurement of pressure, ultrasound, and torsional oscillator to reveal the complete phase diagram. Heat capacity study will also be useful for understanding both phases.

Evidence has also been found for QPT around the critical coverage, n_c, of ^{4}He films in Vycor samples [16]. A theory has predicted that disorder in such porous media results in a QPT between the superfluid and the gapless Bose glass [17]. Therefore, the ^{4}He-Gelsil system may be characterized by two QPTs, at n_c and at P_c.

The small size and disorder of the pore structure may be responsible for the reduction in T_c and $\rho_s(0)$. Since approximately 1.5 ^{4}He atomic layers on the pore walls (up to n_c) are nonsuperfluid, the *real* pore diameter for the superfluid is estimated as 1.5 nm, presupposing ^{4}He hard-core size as being 0.35 nm. There are approximately 20 superfluid atoms in the cross section of the 1.5-nm size pore. This is an order of magnitude smaller than that estimated for Vycor (~ 200 atoms for 6 nm). Because of this extremely small number of atoms, positional exchanges between ^{4}He atoms, which are necessary for possessing superfluidity [18], may be greatly suppressed. This restriction in the exchanges may result in the reduction of T_c to 0 K. Moreover, the exchanges can be disturbed by disorder in the pore structure. In short, the ^{4}He atoms can localize in the pores by correlation and disorder.

It is worth commenting on the marked features in $\Delta f(T)$: (1) The transition in the pressurized states is less sharper than that in the films, and it broadens as P increases. What determines the sharpness? (2) Presupposing a powerlaw for $\Delta f(T)$ at low temperatures, $\Delta f(0) - \Delta f(T) \propto T^{\alpha}$, the exponent α varies from 2.5 at 0.074 MPa to one at 2.64 MPa. This suggests that the dimensionality of phonons varies from 1 (or more) to 0 [19]. Excitation studies, such as neutron scattering [20], are of importance.

In conclusion, we observe a strong suppression of ^{4}He superfluidity by extreme confinement into the nanopores. These results cannot be explained in terms of the conventional concept of superfluid size effect; rather these provide evidence for a novel type of quantum phase transition. ^{4}He-nanopore systems are of prime importance for the pursuit of general problems in strongly correlated bosons in confinement [21].

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