QCM Study of Superfluid Transition in $^4$He Films Adsorbed in SBA-15

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Abstract. A quartz crystal microbalance (QCM) is a useful tool to study the superfluidity of $^4$He films at very high frequencies. Our recent efforts to fabricate mesoporous silica films onto QCM have enabled us to study the noble superfluidity adsorbed in nanopores. In this paper we report results of QCM measurements for the superfluid $^4$He films in SBA-15 with one-dimensional nanopores 4.1 nm in diameter and $\sim 1 \mu$m in length. From the $^4$He pressure isotherm at 4.2 K, a uniform layer is formed in the nanopores up to the coverage of 48 $\mu$mol/m$^2$, corresponding to $\sim 2.5$ layers. The superfluid response is measured at 12 MHz for various coverages in the temperature range of 0.1 – 1.5 K. Above the onset coverage of $\sim 23$ $\mu$mol/m$^2$, we observed a frequency shift accompanied by a dissipation peak due to the superfluid Kosterlitz-Thouless (KT) transition.

1. Introduction

Recently there have been synthesized many kinds of nanopores that have regular void structures and pore diameters which are only a few nanometers. Quantum fluids of helium in these new nanopores are expected to show unique properties in their dimensionality and the correlations [1, 2, 3]. Superfluidity has been studied [1] for $^4$He fluid films adsorbed in 1D tunnel and 3D multiple-connected nanopores $\sim 3$ nm in diameter by heat capacity and torsional oscillator experiments, the superfluid onsets show explicit dependence on the pore connection. In the 1D nanopores, superfluidity was observed in a 1D phonon state where the thermal phonon wavelength was longer than the tube diameter. In the 3D nanopores, the superfluid onset at the heat capacity peak temperature indicates a 3D transition. Our recent efforts to fabricate mesoporous silica films onto a quartz crystal microbalance (QCM) have enabled us to study the noble superfluidity adsorbed in the nanopores. QCM is a candidate for a study of the dynamics of the noble superfluidity in nanopores. In this paper we report results of QCM measurements on the superfluid $^4$He films in 1D nanoporous silicate SBA-15.

2. Experimental

The 1D pore substrate, SBA-15, is made of silica ($\text{SiO}_2$) forming a well-ordered 1D channel structure with a 2D hexagonal (p6mm) symmetry [4]. SBA-15 films are fabricated on a commercial SC-cut quartz disc with a fundamental resonance at 4 MHz and two gold electrodes.
evaporated on its faces. Applying an AC voltage across the two electrodes, the quartz disc, QCM, oscillates with a thickness shear mode as a detector sensitive to the nanogram order of mass. In this study, QCM measurements were done at 12 MHz using 3rd harmonic mode (the harmonic acoustic number \( l = 3 \)). From the N\(_2\) isotherm at 77 K, the SBA-15 has straight channels 4.1 nm in diameter by the Dollimore-Heal (DH) method. The BET surface area is estimated to be 85.9 ± 0.4 cm\(^2\) from the pressure range of 0.05 < \( P/P_0 < 0.3 \), where \( P_0 \) is the saturated vapor pressure, and the magnification factor of QCM sensitivity by the large adsorption surface area of nanopores \( k = 219 \). The pore length is on the order of ∼ 1 µm in length.

The resonant frequency is locked and measured by a DC frequency modulation (FM) technique [5], and decreases proportionally to the mass adsorbed in SBA-15 fabricated on the gold electrodes. A feedback circuit is used to modulate the reference frequency provided by a HP8648B signal generator. This modulated signal acts as the reference for a high frequency lock-in amplifier that monitored the nearly nulled quadrature output of the QCM. The output of the lock-in provides a negative feedback in the form of a DC voltage that is used to lock the circuit to the resonant frequency. Useful information concerning the superfluid dissipation is extracted from the voltage amplitude of the transmitted signal of QCM as the inverse quality factor change \( \Delta Q^{-1} \). The quality factor is determined from the amplitude \( A \) as \( Q = (A/A_0)Q_0 \), where a reference quality factor \( Q_0 \) at an amplitude \( A_0 \) is estimated from the frequency scan at a fixed temperature. The \( Q \) factor at 12 MHz was measured to be 8 × 10\(^4\) at 1 K. The typical excitation voltage \( V \) of QCM was ∼ 1 mV, and the corresponding vibration amplitude was estimated to be ∼ 0.01 nm by \( A \propto QV/l^2 \) [6, 7].

3. Results and Discussion

Vapor pressure measurements are useful to obtain basic information of the film growth inside nanopores. Figure 1 shows the \(^4\)He vapor pressure isotherm of SBA-15 by QCM at 4.2 K, the film thickness calculated by the Frenkel-Halsey-Hill (FHH) model, and two-dimensional isothermal compressibility. The effective film thickness calculated by the FHH model is given by \( \delta = \{\alpha/[T \ln(P_0/P)]\}^{1/3} \), at the temperature \( T \). We assumed that the adsorption coefficient

![Figure 1](image-url)
In this study, the transverse acoustic impedance of the quartz, \( Z_q \), is estimated to be 1.12 MHz, which indicates that the superfluid density is possibly due to the slippage of nonsuperfluid \( ^4\)He films. Observed a complicated temperature dependence of the background frequency and dissipation, which is shown in Fig. 2. In thicker films of \( n \geq 29.1 \mu \text{mol/m}^2 \), the desorption effect is observed above 1 K by the desorption effect.

\[
\alpha = 1100 \text{ KÅ}^3 \quad \text{for a glass substrate} \ [8].
\]

The 2D isothermal compressibility is defined by

\[
\kappa_T = \frac{1}{n^2} \left( \frac{\partial n}{\partial \mu_a} \right)_T = \frac{1}{n^2 k_B T} \left( \frac{\partial n}{\partial \ln P} \right)_T,
\]

where \( n \) is the coverage, \( \mu_a \) the chemical potential of adsorbate, and \( k_B \) the Boltzmann constant. Increasing the coverage, the film thickness \( \delta \) decreases in proportion to \( n \). At \( n_1 \), a sudden increase of the thickness and a decrease in the compressibility are observed. The first layer completion \( n_1 \sim 19.1 \mu \text{mol/m}^2 \) assuming the same atomic area, 0.0869 nm\(^2\), as that of graphite [9]. From the \( ^4\)He pressure isotherm at 4.2 K, a uniform layer is formed in the nanopores up to the coverage of 48 \( \mu \text{mol/m}^2 \), corresponding to \( \sim 2.5 \) layers.

The superfluid response is measured at 12 MHz for various coverages in the temperature range of 0.1 – 1.5 K, as shown in Fig. 2. The coverage is estimated by the usual microbalance method, or the frequency shift from the blank data at 1 K. When the superfluid component in \( ^4\)He films appears, the frequency shift due to the decoupling is

\[
\Delta f_s = -\frac{4k_f_0^2}{1Z_q} \sigma_s (1 - \chi),
\]

where \( \sigma_s \) is the areal superfluid density, \( f_0 \) the initial frequency with no adsorbate, \( Z_q \) the transverse acoustic impedance of the quartz, \( 8.86 \times 10^6 \text{ kg/m}^2\text{s} \), \( l \) the harmonic acoustic number \( (l = 1, 3, 5 \cdots) \), and \( \chi \) the fraction of the superfluid which couples to the substrate. Here, \( f_0 = 12 \text{ MHz} \) and \( l = 3 \). The magnification factor by nanopores is \( k = 219 \) (see section 2). In this study, \( \chi \) is estimated to be \( \sim 0.94 \), and hence the net enhancement of the frequency shift due to the superfluidity is \( \sim 13 \). Above \( n = 24.9 \mu \text{mol/m}^2 \), we observed the frequency shift due to the superfluid transition associated with a broader dissipation peak than the flat gold substrate [10]. The peak temperature of the dissipation is shown by the arrows in the figure. In thicker films of \( n \geq 29.1 \mu \text{mol/m}^2 \), the desorption is observed above 1 K. We also observed a complicated temperature dependence of the background frequency and dissipation, which is possibly due to the slippage of nonsuperfluid \( ^4\)He films at high frequencies [11, 12]. This background frequency change prevents us from extraction of the superfluid density \( \sigma_s \) from the
raw frequency data, and thus we could not discuss quantitatively about the KT universal jump and the broadening for $\sigma_s$.

The coverage dependence of the dissipation peak temperature is shown in Fig. 3. The onset coverage $n_c$ is $\sim 23 \mu\text{mol/m}^2$ ($\sim 1.2$ layers). This coverage dependence is in good agreement with the slope of the Kosterlitz-Thouless (KT) transition temperature [13],

$$T_{KT} = \frac{\pi\hbar^2}{2k_Bm^2}\sigma_s,$$

where $\hbar$ is the Planck constant and $m$ is the mass of $^4\text{He}$ in the region of 25 - 31 $\mu\text{mol/m}^2$. This observation is consistent with the result of FSM-16 with 1D nanopores 4.7 nm in diameter achieved by the low frequency study of the torsional oscillator [2].

4. Conclusion

In conclusion, we report the results of QCM measurements for the superfluid $^4\text{He}$ films in SBA-15 with 1D nanopores 4.1 nm in diameter and $\sim 1\mu\text{m}$ in length. From the $^4\text{He}$ pressure isotherm at 4.2 K, a uniform layer is formed in the pores up to the coverage of 48 $\mu\text{mol/m}^2$, corresponding to $\sim 2.5$ layers. The superfluid response is measured at 12 MHz for various coverages in the temperature range of 0.1 - 1.5 K. Above the onset coverage of $\sim 23\mu\text{mol/m}^2$, we observed a frequency shift accompanied by a dissipation peak due to the superfluid KT transition.

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