Phase diagram of $^4$He adsorbed in 1D 2.4 nm nanopores of FSM

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Abstract. In systematic studies of superfluid $^4$He adsorbed in nanochannels with various diameters, qualitative differences appear in narrow channels below about 2.2 – 2.8 nm, which is likely to relate with the one-dimensional properties of $^4$He superfluid in nanochannels. In order to determine how $^4$He are adsorbed in 2.4 nm channels on the boundary, we have measured the heat capacities down to 0.15 K and determined the phase diagram. Crossover from normal fluid to localized state is observed up to 20 $\mu$mol/m$^2$, larger than 18 $\mu$mol/m$^2$ where the first adsorption layer is completed. And the quantum Bose fluid film is observed above 25 $\mu$mol/m$^2$. The superfluid region observed by a torsional oscillator appears to be inside of this Bose fluid region.

1. Introduction
In order to find out one-dimensional (1D) properties of superfluid $^4$He, systematic studies for $^4$He adsorbed in nanochannels have been done using a family of nanoporous silicates called FSM which have straight nanochannels with various diameters from 1.5 nm to 4.7 nm [1]. The heat capacities of quantum $^4$He films adsorbed in these nanochannels show that the phonon state crossovers to the 1D state at low temperatures where longitudinal excitations are dominant. The crossover temperature becomes lower in wider channels [2], which suggests that the temperature is determined by comparison between the channel diameter and thermal phonon wavelength [3].

In the torsional oscillator experiments, superfluid densities have been observed for $^4$He adsorbed in nanochannels with diameters larger than 1.8 nm [4]. In channels below 2.2 nm, the superfluid fraction is strongly suppressed compared with that above 2.8 nm, and qualitative differences in the temperature dependence and onset coverage are observed. Especially, gradual increase of the superfluid density with decreasing temperature is observed below 2.2 nm. It is likely to relate with the finite-length 1D superfluid which has been extensively studied in recent theoretical works [5–7]. A possible key to understand the whole channel-size dependences of superfluidity of $^4$He adsorbed in nanochannels and their relation with theoretical results is an experimental study of superfluid $^4$He in nanochannels with intermediate diameter 2.4 nm. Therefore, it is required to know how $^4$He are adsorbed in the channel, and in which condition quantum effects appear. This article shows results of heat capacity measurements for $^4$He adsorbed in nanochannels 2.4 nm in diameter. From these results, the phase diagram of the adsorbed $^4$He is determined down to 0.15 K.
2. Experimental details

The nanoporous substrates FSM (Folded Sheets Mesoporous materials) are silicate powders with grain size about 300 nm [8]. The grain has a honeycomb-like structure with straight nanochannels as long as the grain size. The channel diameter is uniform and selectable between 1.5 and 4.7 nm. In this study, FSM (C14) with nanochannels 2.4 nm in diameter was used.

FSM powder is packed into the sample cell with silver powder for good thermal contact. Since the cell is a torsional oscillator for superfluid density measurements with a platform for heat capacity measurements, consistency in coverage is kept between both measurements. Technical details of the heat-capacity measurement with a torsional oscillator are found in Ref. [9]. From estimation by the Brunauer-Emmett-Teller (BET) method for the nitrogen adsorption isotherm at 77 K, the surface area of FSM in the cell was determined as $S_{\text{BET}} = 110 \pm 1 \text{ m}^2$. The coverage $n$ shown in this article was defined as an amount of adsorbed $^4\text{He}$ divided by $S_{\text{BET}}$.

The total heat capacities with the sample cell were measured by the adiabatic heat pulse method down to 0.15 K. The heat capacities of $^4\text{He}$ in FSM channels are estimated by subtraction of the empty cell heat capacity.

3. Results and discussion

Figure 1 shows temperature dependences of the heat capacities $C$ of $^4\text{He}$ adsorbed in 2.4 nm nanochannels as a form of $C/T$. At coverages below 20 $\mu\text{mol/m}^2$, $C/T$ decreases below a temperature $T_L$ indicated by upward arrows in the figure. The shoulder around $T_L$ suggests crossover to the localized state from normal fluid at higher temperatures. $T_L$ lowers with increasing coverage, and then, disappears at 22 $\mu\text{mol/m}^2$, as seen in the figure. Above 25 $\mu\text{mol/m}^2$, more gentle shoulders appear again, which are marked by downward arrows as $T_B$. $T_B$ increases with coverage, and is considered to be onset of quantum effects, as shown later. Similar temperature dependences of the heat capacity are commonly observed for $^4\text{He}$ films adsorbed in FSMS with various channel diameters above 1.8 nm [10,11].

![Figure 1](image1.png)

**Figure 1.** Temperature dependences of the heat capacity of $^4\text{He}$ film adsorbed in 2.4 nm nanochannels. Crossover temperatures $T_L$ to the localized state and onset of quantum effect ($T_B$) are indicated by arrows.

The heat capacity isotherms of adsorbed $^4\text{He}$ are shown in Fig. 2. In these isotherms, the shoulders at $T_L$ and at $T_B$ seen in Fig. 1 correspond to shoulders around 15 $\mu\text{mol/m}^2$ and maxima...
around 25 $\mu$mol/m$^2$ indicated as $n_B$, respectively. In measurements for FSMs with the other channel diameters [10, 11], it has been shown that the heat capacity of $^3$He film continuously increases even above $n_B$. Thus, $n_B$ is considered to be an indication of onset of quantum Bose fluid region which has different quantum statistics from that of Fermi fluid $^3$He.

In Fig. 3, the temperature dependence of $n_B$ (also corresponds to the coverage dependence of $T_B$) is plotted by open circles, together with those for $^4$He in 1.8 and 2.8 nm nanochannels [10, 11]. For the coverages in the horizontal axis, the underlying non-Bose-fluid layer coverages $n_B(0)$, which are respectively estimated by extrapolation of $n_B$ to $T = 0$, are subtracted. As seen in the figure, $n_B$ are almost linear in temperature. Though the slope depends on the channel size apparently, it is considered to be due to narrowing of the channels by the non-Bose-fluid-layer adatoms. Because of the curvature of channels, the effective adsorption area for the fluid-layer adatoms should be smaller than $S_{BET}$ derived by the N$_2$-BET. Solid symbols in Fig. 3 are plotted using the coverages after correction of the adsorption area, given by $[d/(d-2\delta)(n-n_B(0))]$ where $d$ is the channel diameter. Here $\delta$ is the film thickness at $n_B(0)$ and is assumed to be 0.5 nm, referring to vapor pressure results of $^4$He in 2.8 nm nanochannels [12]. As a result, all $n_B$ are collapsed into the solid line in the figure, which is the temperatures where the thermal de Broglie wavelength of adatoms $\lambda_T = \sqrt{2\pi \hbar^2/mk_BT}$ exceeds 1.8 times the mean interatom distances of fluid layer $a = [(n-n_B(0))N_A]^{-1/2}$ ($N_A$ is Avogadro’s number). It is known that when $\lambda_T$ becomes about 1.8a, the heat capacity of ideal 2D Bose gas also crossovers from the gas constant for classical gas to $T$-linear one of quantum degenerate gas. This result suggests that first around $T_B$, the quantum effect appears in the 2D fluid layer by overlapping of wave packets, and then dimensionality of the collective modes, phonons, is determined by comparison between the wavelength and channel diameter. At low temperatures, phonon excitations crossover to the 1D state, as observed in previous measurements [2, 3].

Figure 3. Temperature dependences of $n_B$, or coverage dependences of $T_B$ for $^4$He film adsorbed in nanochannels with various diameters. $n_B(0)$ is the coverage of background non-Bose-fluid layers. While coverages for open symbols are estimated from $S_{BET}$, solid symbols are plotted by coverages corrected on the surface area (see text). Below the solid line, the thermal de Broglie wavelength $\lambda_T$ of $^4$He becomes longer than 1.8 times the fluid-layer mean interatom distance $a$.

The isotherms between 0.3 and 0.7 K in Fig. 2 have plateaus between 15 and 18 $\mu$mol/m$^2$. Above 18 $\mu$mol/m$^2$, the heat capacity increases steeply again. This increase is considered to be due to the heat capacity of adatoms promoted into the second adsorption layer. Thus it suggests that the coverage $n_1$ of the first adsorption layer completion is about 18 $\mu$mol/m$^2$. Though such a kink at $n_1$ in the isotherm was not clearly observed for $^4$He in the other channel-size FSMs [10, 11], the precise measurement shown here enables us to determine it. In addition, upturns by heat of desorption can be seen above 30.5 $\mu$mol/m$^2$ in the isotherms. From the analysis of the vapor pressure at 4.2 K similar to the shown in Ref. [12], it has been confirmed that $^4$He film in 2.4 nm nanochannels grows uniformly up to a coverage $n_f \sim 30 \pm 2$ $\mu$mol/m$^2$. The appearance of desorption is likely to accompany the change in adsorption above $n_f$ [9], and suggests $n_f \sim 30.5$ $\mu$mol/m$^2$. The ratio $n_f/n_1$ is estimated to be 1.7 which is a reasonable value, compared to 1.7 in 2.2 nm channels and 2.0 in 2.8 nm [13].

From these analyses, the phase diagram of $^4$He adsorbed in FSM with 2.4 nm nanochannels...
has been determined as shown in Fig. 4. In the diagram, superfluid onset temperatures $T_S$ measured by the torsional oscillator are also plotted. The slope of $T_S$ becomes steeper above $n_f$, reflecting change in $^4$He adsorption suggested by upturns in the heat capacity isotherms. In this diagram, it can be seen that the region where superfluidity is observed is completely inside of quantum Bose fluid region determined by the heat capacity measurement.

**Figure 4.** Phase diagram of $^4$He adsorbed in 2.4 nm nanochannels. Crossover temperatures $T_L$ to the localized state are extracted from Fig. 1. Onset coverages $n_B$ of quantum Bose fluid, $n_1$, and $n_f$ are derived from Fig. 2. In addition, superfluid onset temperatures observed by the torsional oscillator are plotted as $T_S$.

4. Summary

We have measured the heat capacity of $^4$He adsorbed in nanochannels 2.4 nm in diameter, and determined the phase diagram. From anomalies observed in the temperature dependence and isotherms of the heat capacity, we have found the coverage $n_1 = 18 \mu$mol/m$^2$ of the first-layer completion, the upper-limit coverage of uniform film growth $n_f \sim 30.5 \mu$mol/m$^2$ (1.7$n_1$), crossover temperatures $T_L$ to the localized state, and onset coverages $n_B$ (or temperatures $T_B$) of quantum Bose fluid. For a next step, crossover to the 1D phonon state should be determined by the heat capacity measurement at lower temperatures.

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