Amorphous solid like heat capacity of $^4$He fluid films adsorbed on pores

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Abstract. In the nanopores of HMM-2 whose mean pore diameter is 2.7 nm, adsorbed $^4$He forms layers up to about two atomic layers. At low temperatures, the $^4$He films show properties of the Bose quantum fluid and superfluidity above about 1.4 layers. Below the coverage or above the superfluid transition temperature, $^4$He film is in the normal fluid state. The heat capacity of the normal fluid shows linear temperature ($T$) dependence. The $T$-linear coefficient of the heat capacity is about $5 \mu J/(m^2 \cdot K^2)$. According to Andreev’s idea originally developed for bulk helium liquids, the $^4$He fluid can be regarded as an amorphous solid with $T$-linear dependence of the heat capacity. Its coefficient is described as $\pi^2 D_0 k_B^2 / 6$, where $D_0$ is a density of states and $k_B$ is the Boltzmann constant. The density of states is estimated from the density (coverage) dependence of the isosteric heat of sorption $q_{st}$ which was obtained from the vapor pressure data of adsorption. The estimated density of state well explains the observed magnitude of the $T$-linear coefficient of heat capacity.

1. Introduction
Bulk $^4$He liquid is a typical example of Bose fluid. F. London compared its superfluid transition temperature (2.19 K) with the Bose-Einstein condensation temperature (3.13 K) of a three-dimensional (3D) ideal gas. But, some correspondences are not sufficient, because there are interactions between $^4$He atoms. To explain the specific heat of the normal $^4$He liquid that is quite different from that of the Boltzmann gas, Andreev has proposed a semi-quantum liquid model where the $^4$He liquid is regarded as an two-level quantum tunneling system rather than an ideal gas [1]. We have realized $^4$He fluid films adsorbed on walls of the nanopores that have regular 1D and 3D structures [2]. In the 3D nanopores, the $^4$He films show the 3D superfluid transition; the heat capacity shows a peak at the superfluid onset temperature $T_S$. The coverage (density) dependence of $T_S$ is well reproduced as the BEC temperature of the 3D Bose gas, even though the magnitude of the specific heat is not equal to that of the 3D gas. The overall properties should be studied for the new $^4$He fluid films.

In this paper we studied the normal state of the $^4$He fluid films adsorbed in 3D nanopores of HMM-2 where the pores 2.7 nm in diameter are connected in three-dimension. We observed that the heat capacity of the normal fluid films show a linear temperature ($T$) dependence which is similar to that of the bulk $^4$He normal liquid. Thus, the heat capacity is analyzed in terms of the semi-quantum liquid model. Density of states obtained from the $T$-linear term is compared with

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that obtained independently from the coverage dependence of the adsorption energy (isosteric heat of sorption) from the vapor pressure data.

2. Structure and properties of $^4$He films formed in HMM-2
The nanopore substrate HMM-2 is made of ethanesilica units (O$_{1.5}$Si-CH$_2$CH$_2$SiO$_{1.5}$) with a 3-d hexagonal ($P6_3/mmc$) pore structure [3]. The pores 2.7 nm in diameter (the BJH method) are connected in three-dimension with a regular 3D period of 5.5 nm. The specific surface area of the nanopores is 1270 m$^2$/g which is estimated from the N$_2$ pressure isotherm at 77 K (the BET method). Our experimental cell has the adsorption area of 79 m$^2$.

The nature (structure, energy, ···) of the adatoms was studied by thermodynamic analyses of the vapor pressure measurements of adsorption [4]. The analysis by the Frenkel-Halsey-Hill model indicates that a uniform layer (film) on the nanopore walls is formed of up to $n_f$. The first layer is indicated by the minimum of $\kappa_T$ as shown in Fig. 1(a). Completion of the first layer is obtained from vapor pressure for the adsorption. The first layer is completed at $n_1$, and a uniform layer is formed up to $n_f$.

![Figure 1](image1.png)

**Figure 1.** Two-dimensional isothermal compressibility $\kappa_T$ (a) and isosteric heat of sorption $q_{st}^0$ (b) of $^4$He adsorbed in HMM-2, obtained from vapor pressure for the adsorption. The first layer is completed at $n_1$, and a uniform layer is formed up to $n_f$.

![Figure 2](image2.png)

**Figure 2.** Heat capacity $C$ of $^4$He divided by $T$ in various coverages $n$. At low coverages, the adatoms are localized below $T_L$. At $n > n_c$, superfluid was observed below $T_S$. In the normal fluid states above $T_L$ or $T_S$, $C$ is well fitted by $C = a_1 T + a_2 T^2$, as shown by solid lines.

3. Heat capacity of adsorbed $^4$He in normal fluid state
From heat capacity $C$ and superfluid measurements, we determined the phase diagram of $^4$He adsorbed in HMM-2 [2]. Figure 2 shows the heat capacity data, plotting $C/T$ against $T$. At low coverages below $n_c \approx 21$ µmol/m$^2$, $C/T$ shows a sudden decrease below a temperature $T_L$, this
was concluded to be a localization state of the adatoms below $T_L$. $T_L$ decreases with increasing $n$. At the higher coverages, $C/T$ shows another kind of decrease below $T_S$ where a small but sharp peak was observed. At the same temperature, we observed the superfluid onset by the torsional oscillator. $T_S$ increases with $n$ or density, which is well reproduced by the calculation of the BEC temperature for the 3D ideal Bose gas. The phase above $T_L$ or $T_S$ is likely to be in a normal fluid state.

The heat capacity $C$ of the normal fluid state can be well fitted by the form $C = a_1 T + a_2 T^2$, as shown by the solid lines in Fig. 2. The coverage dependences of $a_1$ and $a_2$ are shown in Fig. 3. At the low coverages, the $T$-linear term is sufficiently larger than the other term at lowest temperature or just above $T_L$. At the higher coverages, the $T^2$-term above $T_S$ increases with $n$ in contrast to the decrease of the $T$-linear term, although $C/T$ obviously increases with $n$. Typical magnitude $a_1$ of the observed $T$-linear term is $5 \mu J/(m^2 K^2)$ at $n = 17 \mu mol/m^2$. The coefficient per one mole is $a_1/n \approx 0.3 J/(mol K^2)$. Similar $T$-linear heat capacity was observed for the $^4$He films formed in Y-Zeolite [5]. Its $T$-linear coefficient $(a_1/n)$ is the same order as that of $^4$He adsorbed in HMM-2. Both $T$-linear heat capacities are likely to correspond to that of the bulk $^4$He normal liquid, as described in the next section.

4. Amorphous-solid (glass) model for $^4$He fluids
For the semi-quantum fluids of $^4$He, $^3$He and H$_2$ whose de Boer parameters are large, the heat capacities in the normal fluid state do not correspond with those of the non-interacting Boltzmann gas. Andreev pointed out that the normal fluids show the $T$-linear heat capacity, and explained it by regarding the fluid as an amorphous-solid (glass) [1]. The semi-quantum fluid can be seen as a solid when $T$ is sufficiently lower than the Debye temperature. The $T$-linear heat capacity of the amorphous solids was explained by a two-level-system model assuming quantum tunneling between different states. The coefficient $\alpha$ is given by $\alpha = \pi^2 D_0 k_B^2 \Theta_D^2 / 6$, where $D_0$ is the density of states. The superfluid transition of the $^4$He fluid occurs at the condition $k_B T_S \approx \hbar^2 \tau$, where $1/\tau$ is the quantum tunneling rate. Thus, the semi-quantum fluid shows the $T$-linear heat capacity at $T_S \ll T \ll \Theta_D$. In the case of the bulk liquid $^3$He at 25 atm whose Debye temperature is $\Theta_D = 32.7$ K and the superfluid transition $T_S \sim 1.7$ K, the $T$-linear heat capacity with the coefficient $\alpha \approx 2 J/(mol K^2)$ is observed between 3 and 10 K.

Analyzing the vapor pressure data for adsorption, we actually obtained the 2D isothermal

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Figure 3. $n$-dependence of the coefficients of the temperature dependence of heat capacity on the formulation $C = a_1 T + a_2 T^2$ above $T_L$ or $T_S$.

Figure 4. $a_1$ of the $T$-linear heat capacity term of the normal fluid (see the text), $\alpha$ (solid line) of the $T$-linear heat capacity estimated from the pressure data, and the Debye temperature $\Theta_D$. 

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compressibility $\kappa_T$ and the work function $q_{st}^0$ of the $^4$He films adsorbed in HMM-2, as shown in Fig. 1(a) and (b), respectively [4]. From $\kappa_T$ and assuming that it is equal to the adiabatic compressibility $\kappa_S$, we can obtain the phonon velocity by $v = \sqrt{\frac{1}{mn\kappa_S}}$, where $m$ is the mass of $^4$He atom. The value of $v$ is about 350 m/s at $n_1$ which is close to the value of bulk $^4$He liquid near the melting pressure [6]. The phonon velocity gives the Debye temperature of the $^4$He films by $\Theta_D = \frac{hv}{k_B} \sqrt{\frac{\pi}{n}}$ which are shown in Fig. 4. Since $\Theta_D$ is the order of 20 K, the $^4$He films formed in HMM-2 can be regarded as an amorphous solid sufficiently below 20 K. The isosteric heat of sorption $q_{st}^0$ (Fig. 1(b)) is the minimum energy to bring a $^4$He adatom to the free space (vacuum). In the semi-quantum fluid model, the energy band is filled below the energy $-q_{st}^0$ at $T = 0$ K at which the density of state is $D_0$. This indicates the following relation: $D_0 = (-\Delta q_{st}/\Delta n)^{-1}$. From the coverage $n$ dependence of $q_{st}^0$, we calculated $D_0$ and the coefficient $\alpha = \pi^2 D_0 k_B^2 / 6$ of the $T$-linear heat capacity, as shown by the solid line in Fig. 4. $\alpha$ obtained from the pressure data well agrees with $a_1$ of the $T$-linear heat capacity term at the coverages below $n_c$. Since the superfluid transition temperature $T_S$ observed above $n_c$ increases with the coverage, $a_1$ of the $T$-linear term is not determined in the condition $T_S \ll T \ll \Theta_D$ that is requested in the model. The reasonable agreement shown in Fig. 4 suggests that the normal fluid state of the $^4$He films formed in HMM-2 can be described by Andreev’s amorphous solid model.

5. Summary
The $^4$He properties, i.e., the layer formation, the 2D compressibility $\kappa_T$ and the isosteric heat of sorption $q_{st}$, adsorbed in the 3D nanopores of HMM-2 were obtained by the thermodynamic analyses of the vapor pressure measurements of adsorption. The 3D superfluid transition of the $^4$He films observed above 1.4 layers was well understood in terms of the Bose-Einstein condensate of the 3D Bose gas. However, the heat capacity in the normal fluid state is not that of the ideal Boltzmann gas. The $T$-linear dominant heat capacity of the normal fluid can be explained as an amorphous solid (glass) heat capacity proposed firstly for the bulk $^4$He normal liquid. The Debye temperature and the density of states requested in the amorphous solid model to explain the heat capacity results agree rather well with those calculated from $\kappa_T$ and $q_{st}$ obtained from the pressure data. Thus, the $^4$He fluid films as well as the bulk liquids in the normal states can alternatively be regarded as the amorphous quantum solid with many vacancies.

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