Phase Diagrams of $^4$He Bose Fluids Formed in One- and Three-Dimensional Nanopores

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Abstract. In the one-dimensional (1D) nanopores of FSM-16 (2.8 nm in diameter) and the 3D pores of HMM-2 (2.7 nm, and 5.5 nm in 3D period), the $^4$He films adsorbed on these nanopore walls show the properties of the Bose quantum fluid and superfluidity above 1.4 atomic layers at low temperatures. The boundary of the Bose fluid region was determined from the kink (peak) temperature $T_C$ of the heat capacity at each coverage $n$. The phase diagrams obviously show dependence on the 1D and 3D pore connections, respectively. In the 3D nanopores, the coverage (density) dependence of $T_C$ is well reproduced by the Bose-Einstein condensation temperature of the 3D ideal gas which is proportional to $(n - n_c)^{2/3}$, where $n_c$ is the onset coverage. In the case of the 1D pores (channels), $T_C$ is proportional to $(n - n_c)$ at $0.1 < T_C < 1$ K. This $T_C$ is likely to correspond to the crossover temperature of the 2D ideal gas heat capacity from the constant heat capacity of the Boltzmann gas to the linear in $T$, with decreasing temperature. At $T_C$, the thermal de Broglie wavelength of the free particle is still shorter than the pore diameter, while the thermal phonon wavelength is estimated to become longer than the diameter below $T_C$, which indicates the 1D phonon state.

1. Introduction

Following the first liquefication of helium, helium quantum fluids have been widely explored under the extreme condition of low temperature. Other unique properties have been studied for films adsorbed on flat solid surfaces [1] and in Vycor glasses [2]. Under new nano-extreme conditions realized in nanopores where a few nm pores form regular structures, we have been studying the $^4$He and $^3$He fluids that are expected to reflect the dimensionality of the pore connection as well as the interactions between the adatoms and the substrates.

In this paper we studied the dimensionality of the $^4$He fluid films formed in 1D and 3D nanopores that have the same pore diameter and substrate potential, except for the different 1D and 3D pore connections. The phase diagrams determined from the heat capacity and superfluid measurement by the torsional oscillator are compared with the ideal Bose gases in various dimensions.

2. Phase diagrams of $^4$He in 1D and 3D nanopores

The 1D and 3D nanopores used in the present experiments are shown in the insets of Figs. 1(a) and (b), respectively. The 1D channels 2.8 nm in diameter are formed in a honeycomb frame

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Figure 1. Frequency shift $\Delta f$ by the superfluid and heat capacity $C$ divided by $T$ for $^4$He adsorbed in (a) 1D (2.8 nm) pores and in (b) 3D (2.7 nm) pores, respectively.

Figure 2. Phase diagrams of $^4$He in (a) 1D and (b) 3D nanopores. Kink (peak) of heat capacity at $T_C$ give the boundary of the B-phases. $T_S$ is the superfluid onset temperature.

about 300 nm in size. The 3D network of the pores 2.7 nm in diameter is made in the regulat frame with a hcp symmetry and the 3D period 5.5 nm. The adsorption energies on these nanopore walls are almost the same at about 110 K for $^4$He. Thus, they have the same pore diameter and adsorption potentials, except for the dimensionality of the pore connectivity.

On these nanopore walls, uniform $^4$He layers are formed up to two atomic layers ($n_f/n_1 \approx 2$). A fluid state depending on the adatoms’ quantum statistics was identified by measuring heat capacity $C$ of $^3$He as well as $^4$He. Qualitatively different heat capacities between the two isotopes indicates the fluid states above about $1.4 n_1$. Considering the approximate thickness of the inert layers, about 0.5 nm, the fluid film tube diameters are about 1.8 and 1.7 nm for the 1D and 3D nanopores, respectively. Isotherm of the $^4$He heat capacity shows a peak at a coverage $n_B$ above which we can expect the Bose-Einstein condensate (BEC) and/or the superfluid. We call this region the B-phase in this paper. Corresponding to the boundary of the B-phase, temperature dependence of the heat capacity has a kink (peak) at $T_C$, as shown in Figs. 1(a) and (b) [3]. From $n_B$ and $T_C$ the phase diagrams for the B-phases are determined, as shown in Figs. 2(a) and (b) for 1D and 3D nanopores, respectively. For the 1D pores, $T_C$ increases in proportion to $n$. $T_C$ for the 3D pores shows the 2/3-power law against the fluid density, $n - n_{c'}$, followed by the tail near the onset coverage, as discussed below. The low temperature heat capacities in each B-phase can be analyzed by a phonon heat capacity model [4], which determines the phonon velocities $v$ and, in the 1D pores, the gap energy $\Delta$ between the ground state and the first excited state in the transverse motion of the fluid tube. These phonon parameters define the dimensionality for the thermal phonon excitations in the B-phases. In the 1D pores, the B-phase below about 0.8 K is in the 1D phonon state where the thermal phonon wavelength $hv/k_B T$ is longer than the fluid tube diameter 1.8 nm, as well as $k_B T < \Delta$. In the 3D pores, the B-phase below 1 K is in the 3D phonon state where $hv/k_B T$ is longer than the 3D period 5.5 nm.

In order to study the superfluidity in these B-phases, we measured the superfluid by the torsional oscillator and the heat capacity at exactly the same coverage [3]. In the case of the 1D
pores (2.8 nm) (Fig. 1(a)), superfluid onset is observed at $T_S$ far below $T_C$ which is the boundary of the B-phase at the coverage $n = 26.5$ μmol/m$^2$. $T_S$ is plotted by a solid diamond in Fig. 2(a). The superfluid observed S-phase is at low temperatures below the B-phase boundary. On the other hand, in the 3D pores (2.7 nm) (Fig. 1(b)), the superfluid onset was observed at the same temperature on the boundary of the B-phase ($T_S = T_C$), within the experimental uncertainties. This is clear evidence of the 3D superfluid transition. The qualitatively different phase diagrams (Figs. 2(a) and (b)) must be due to the dimensionality of the pore connectivity [3].

3. Comparison with Bose gas heat capacities in various dimensions

![Figure 3](image)

Specific heats $C/n$ of Bose gases from 3D to 1D are calculated as shown in Fig. 3, in which $R$ is the gas constant, and $T$ is normalized for $T_0$ where the thermal de Broglie wavelength $\lambda_T = h/\sqrt{2\pi m k_B T_0}$ is equal to the mean particle distance. $C/nR$ of the 3D Bose gas shows a peak at the condensation temperature $T_{3D-BEC}/T_0 = 0.51$. It is also described as $T_{3D-BEC} = \frac{2\sqrt{2} m \lambda_T}{k_B T_0 (N_A n_{3D})^{2/3}}$, where $m$ is an atomic mass, $N_A$ is Avogadro’s number and $n_{3D}$ is the 3D gas density. It is well known that the 2D and 1D Bose gases do not set into BEC at finite temperature. However, $C/n$ of the 2D Bose gas shows the crossover from $R$ of the 2D Boltzmann gas at high temperatures to the $T$-linear dependence at the temperature $T_{2D} = 0.28 \pm 0.05$, as shown in Fig. 3. Hence, $T_{2D}$ is proportional to the 2D density $n_{2D}$ in the rate $(0.13 \pm 0.02)$ K/(μmol/m$^2$).

The 3D superfluid transition of the bulk $^4$He liquid was attributed to BEC of the 3D Bose gas by F. London, because the condensation temperature $T_{3D-BEC} = 3.2$ K calculated for the same density gas is the same order as the lambda temperature 2.2 K. Observing the heat capacity peak at the superfluid onset temperature, 3D superfluid transition was first suggested for the $^4$He fluid films adsorbed on the pore walls of porous Vycor glasses, where the pores are about 7 nm in diameter and are connected randomly in 3D, with the mean period of the order of ten nanometers [5]. The coverage dependence of the superfluid transition temperature $T_S$ was quantitatively well explained by BEC of the 3D ideal Bose gas, by assuming the effective mass was 1.3 times the bare $^4$He mass [2]. In the present 3D nanopores, 5.5 nm in regular 3D period, the $^4$He films show the explicit properties of the 3D transition; the superfluid onset occurs at the heat capacity peak temperature ($T_S = T_C$). The coverage $n$ dependence of $T_C$ (Fig. 2(b)) is well fitted with $T_{3D-BEC}$ of the 3D Bose gas, as shown by the solid curve. Here, we assume the bare $^4$He atomic mass $m$ and the 3D gas density $n_{3D} = 8.26 \times 10^8$ [m$^{-1}$] ($n = n_{3D}$) [μmol/m$^2$], where the fluid $(n - n_{c})$ on the inert layer of $n_{c} = 22.4$ μmol/m$^2$ is homogeneously averaged within the total volume of the substrate frame and the void. The calculated $T_{3D-BEC}$ well reproduces the $2/3$-power law of the B-phase (S-phase) boundary above about 0.15 K. The deviation near the onset coverage $n_{c} \approx 21$ μmol/m$^2$ may be due to the increase of the inert layer coverage from $n_{c}$ to $n_{c'}$ by the promotion of the fluid layers or perhaps due to the Bose glass transition. The heat capacity has a small but sharp peak at $T_C$ (Fig. 1(b)), although the
magnitude of the specific heat is smaller than that of the 3D Bose gas (Fig. 3). The observed superfluid density below $T_C$ is well reproduced by that calculated for a 3D atomic gas [3].

In contrast to the 2/3-power law for the 3D pores, $T_C$ of the B-phase boundary for the 1D pores increases in linear proportion to $n$ (Fig. 2(a)). So, $T_C$ can be compared with the crossover temperature $T_{2D}^{c}$ of the 2D Bose gas heat capacity (Fig. 3). Since $\lambda_T$ is smaller than the circumference of the 1.8 nm tube even at the lowest measured temperature ($\approx 0.1$ K), the fluid film seems to be a 2D free particle gas at $T_C$. In Fig. 2(a), $T_C$ of the B-phase boundary changes at the rate $0.18$ K/(\mu mol/m$^2$). Considering the reduction of the tube adsorption area from the 2.8 nm 1D pore to the 1.8 nm fluid tube, the rate should be corrected from 0.18 to 0.12 K/(\mu mol/m$^2$), in order to compare with $T_{2D}^{c}/n_{2D} = (0.13 \pm 0.02)$ K/(\mu mol/m$^2$) of the 2D ideal gas (Fig. 3). The agreement is within the uncertainty in the adsorption area.

At the B-phase boundary below about 0.8 K, the $^4$He fluid film nanotube is estimated to be in the 1D phonon state, where the thermal phonon wavelength is longer than the tube diameter (about 1.8 nm) [3]. The superfluid was observed far below $T_C$ (Figs. 1(a)), and the observed superfluid density shows a rather steep increase below $T_S$ [3]. At the same time, we observed a dissipation of the torsional oscillator. These are rather similar properties to the KT transition, and completely different from those of the films formed in the 3D nanopores.

4. Conclusion
Phase diagrams of $^4$He for the quantum Bose fluid state and superfluid are determined by the heat capacity and the torsional oscillator experiments for the 1D and 3D nanopores which have the same pore diameters and adsorption potentials with the exception of different 1D and 3D pore connections, respectively. In the 3D pores, the $^4$He fluid films show the 3D superfluid transition. The coverage (density) dependence of the transition temperature is well reproduced by the BEC temperature of the 3D ideal Bose gas. For the 1D pores, the boundary of the B-phase determined by the heat capacity can be explained as the crossover temperature of the 2D Bose gas heat capacity from the constant of the Boltzmann gas to the $T$-linear dependence in the quantum region. The superfluid is observed far below the B-phase boundary in the 1D phonon state.

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