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# Heat capacity of thin films of $^3$He adsorbed on a heterogeneous substrate

Andrei Golov* and Frank Pobell
*Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany*

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We have measured the heat capacity of $^3$He films on porous Vycor glass at $10 \leqslant T \leqslant 600$ mK. As the coverage is increased from 1 to 3 atomic layers, the heat capacity evolves from that typical to solid to that of liquid $^3$He, being weakly temperature dependent at thicknesses of about two layers. A model is proposed of a gradual ordering of spins in an amorphous $^3$He film, suggesting a broad uniform distribution of the logarithm of exchange parameters. It yields a constant heat capacity of about 13 $\mu$J/K m$^2$, which is close to the experimental results for $^3$He films on silver and Vycor.

Adsorbed $^3$He films are good model systems to study the properties of strongly correlated fermions in reduced dimensions or in the presence of disorder. Considerable progress has been achieved in the study of $^3$He films adsorbed on homogeneous substrates like Grafoil.[1–4] Dependent on the density, the first and second $^3$He layers on Grafoil demonstrate examples of a homogeneous two-dimensional (2D) Fermi liquid and a 2D quantum crystal. But for the case of $^3$He in contact with rough substrates like silver powder, some evidence has been reported of a temperature-independent heat capacity of unknown origin.[5,6] In this paper we discuss the influence of the disordered potential of extremely rough substrates on the heat capacity of $^3$He films. For such a study, Vycor (porous glass Corning 7930) seems to be an appropriate substrate. Experiments have shown that its surface is very rough, containing irregularities on the scale of 10–100 Å.[7] $^4$He films on Vycor have been studied in detail,[8–12] and we believe that their structure could be similar to that of $^3$He films on Vycor. At coverages above 16 atom/nm$^2$ $^4$He films demonstrate superfluidity.[11,12]

Condensed helium is highly compressible, and the attractive van der Waals potential of the substrate is of very short range. Hence, the old ''statistical layer'' model for liquid $^3$He on Vycor considers three parts:[8] a first solid layer of $^3$He strongly bound to the substrate having interatomic distance $a \simeq 3.3$ Å (coverage $N_1 \approx 11$ atom/nm$^2$); a second moderately compressed layer ($a \simeq 3.8$ Å, $N_2 \approx 8$ atom/nm$^2$) which usually was treated as having the properties of a homogeneous bulk liquid with $a \simeq 3.8$ Å, i.e., liquid $^3$He under the pressure of about 35 bar; the remaining adsorbed $^3$He having the properties of bulk liquid $^3$He at zero pressure ($a \simeq 4.4$ Å).

Such a model works well for the density of $^3$He films, but fails in the case of other properties, such as specific heat.[8] This is because the ''second statistical layer'' of $^3$He does not behave as bulk liquid $^3$He at all. The idea of layers would probably work for the case of a smooth substrate where homogeneity in the plane of the substrate still exists. However, on a rough substrate there are no well-defined atomic layers, but rather different atomic positions with a continuous distribution of energy of adsorption. As we will show below, the heat capacity of the main part of the ''second layer'' looks not like that of a homogeneous liquid, but rather like that of a disordered solid. Due to a short-range inhomogeneity in every direction, the growth of a 2D crystalline phase with a long-range order is forbidden. Therefore, we refer to those solid regions of the film (with localized He atoms) as *amorphous solid*. For instance, NMR study of such amorphous $^3$He films in contact with rough substrates[13,14] revealed an extremely broad continuous distribution of exchange parameters $J$ instead of sharply peaked values, which would be typical for a crystalline state.

Greywall and Busch[5] have found that the heat capacity of the second layer of $^3$He on silver powder is different than that on Grafoil. It was found to be almost temperature-independent between about 1 mK and the highest temperature studied, 7 mK. Increasing the coverage above 14 atom/nm$^2$, its value saturated at about 13 $\mu$J/K m$^2$ and this number was not influenced by adding further fluid overlayers. Because of its relatively high heat capacity, they have concluded that the second layer is liquid and tried to interpret the data in terms of a 2D homogeneous nondegenerate Fermi liquid. However, for the partially filled second layer of $^3$He, this approach suggests a very low degeneracy temperature $T_D < 10$ mK, even though on Grafoil this is found to be typically $T_D \geqslant 200$ mK.[1,4] In this paper, we introduce a different interpretation of the temperature-independent term based on a treatment of the spin entropy of $^3$He atoms in the amorphous solid parts of the films.

For our experiments, a rod of Vycor glass (0.37 cm diam, 2.25 cm long) has been cleaned by successive boiling in $H_2O_2$ and $H_2O$, and then dried with silica gel and in a vacuum oven. Then a silver foil with a resistive heater has been glued around the rod. One side of the rod was fit into a silver holder with filling capillary, carbon resistance thermometer, and indium heat switch. The Vycor rod and the silver holder were cast together in epoxy. For the heat capacity measurements, the duration of the heat pulses was typically 20 to 40 sec, the relative temperature increments were in the range 5–10 % at low temperatures and about 20–30 % at $T > 0.5$ K. The time constant for temperature equilibration did not exceed 1 min. The heat capacity of the calorimeter was measured independently and subtracted from the data. Presented here are only those data which are higher than 50% of the addendum.

Measurement of BET (Brunauer-Emmett-Teller, see Ref. 8 for details) adsorption isotherms with $N_2$ at 77 K yield a

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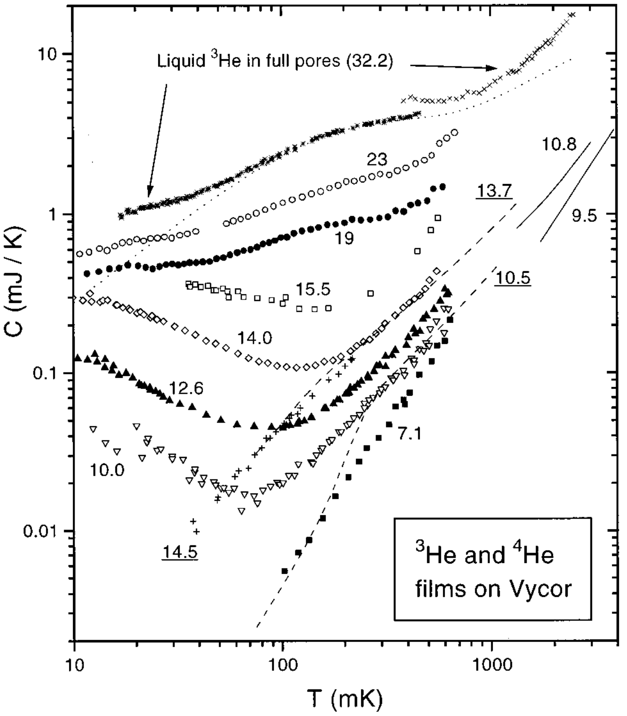

FIG. 1. Temperature dependence of the heat capacities of $^3$He and $^4$He films on Vycor glass. Two upper curves correspond to liquid $^3$He in full Vycor pores and zero pressure [$*$, our data; $\times$, from Ref. 17, and for comparison, the dotted line to the bulk liquid $^3$He (Ref. 16) of volume 0.045 cm$^3$]. Crosses $(+)$ correspond to a $^4$He film of coverage 14.5 atom/nm$^2$ (our data). Solid (dashed) lines represent scaled data for $^3$He films from Ref. 9 ($^4$He films from Ref. 11). Coverages are given in atom/nm$^2$; normal font indicates $^3$He; underlined indicates $^4$He.

surface area 49 m$^2$ for the Vycor sample (using the value of 16.2 Å$^2$ per molecule) and an open volume 0.080 cm$^3$. Before admitting doses of $^3$He gas, the cell was evacuated for 9 h at high temperature. The $^3$He films were annealed at about 4.2 K for at least 10 h. The heat capacity data were very reproducible over the periods up to 14 days at low temperature. Due to the relatively large cold volume of the filling capillary, there was some uncertainty in the determination of the amount of adsorbed helium at coverages higher than 14 atom/nm$^2$; they are given only approximately, to an accuracy of about 10%, for the thickest films.

The temperature dependences of the measured heat capacities are shown in Fig. 1 along with some scaled data for $^3$He and $^4$He on Vycor from previous studies.[9,11,17] At low coverages the data resemble the specific heat of solid $^3$He with its high-temperature spin-independent vibrational contribution and a low-temperature nuclear exchange contribution. The high-temperature contributions for thin films of both $^4$He and $^3$He on Vycor are essentially the same at same coverages and could be fit by $AT+BT^2$ temperature dependence. The quadratic term is generally attributed to a quasi-2D phonon contribution,[8,9] while the linear term is attributed to a kind of ''normal liquid'' excitations, which can be activated at temperatures higher than some coverage-dependent threshold[11,12] (see Ref. 15 for more details and discussion).

For coverages above 14 atom/nm$^2$ the low-temperature part of the heat capacity flattens to a value of the order of 0.5 mJ/K. Only after some 19 atom/nm$^2$ is there a clear indication of an appearance of the contribution of bulklike liquid $^3$He with a typical shoulder at about 200 mK due to spin ordering. This is emphasized in Fig. 1 by the dotted line corresponding to the heat capacity of 0.045 cm$^3$ of bulk liquid $^3$He at zero pressure[16] (0.045 cm$^3$ being the central volume of pores in our sample, calculated as the open volume 0.080 cm$^3$ minus the volume of first two surface layers of the total thickness 7.1 Å). The high-temperature data of Brewer *et al.*[17] for liquid $^3$He in full pores (scaled to the coverage 32.2 atom/nm$^2$ using the number of saturated coverage of 1.20 cm$^3$ at STP/m$^2$ from Ref. 8) is also in a fairly good agreement with our data. Our study and analysis of the heat capacity of liquid $^3$He in Vycor are reported briefly in Ref. 18.

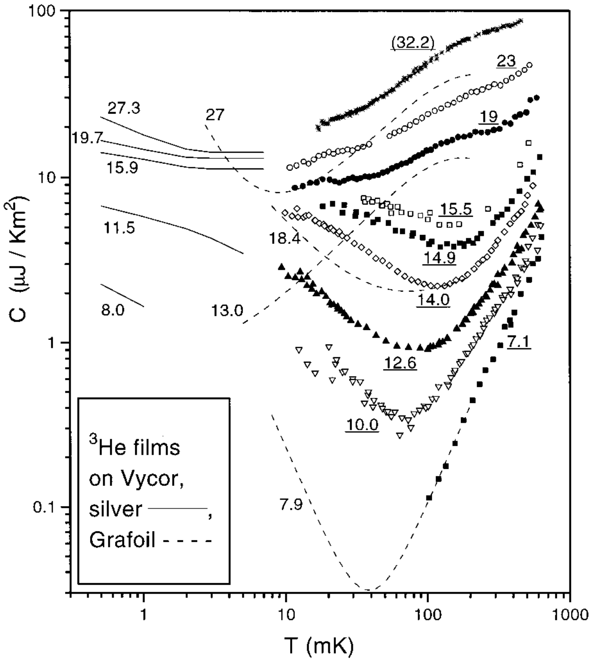

FIG. 2. Comparison of the heat capacity of adsorbed $^3$He films on different substrates (per m$^2$ of the substrate area). Coverages in atom/nm$^2$ are indicated. Symbols: on Vycor (our data, coverages are underlined); solid lines: on silver powder (Ref. 5); dashed lines: on Grafoil (Ref. 1).

Let us compare our results to the data for $^3$He films on other substrates. The symbols shown in Fig. 2 correspond to our data on Vycor, the solid lines are for $^3$He on silver,[5] and the dashed lines are for $^3$He on Grafoil.[1] In contrast to the measurements on Grafoil, for a partially filled second layer of $^3$He (coverages 11–13 atom/nm$^2$), in our data there is no indication of a Fermi-liquid specific heat linear in temperature. Our observed gradual evolution of the heat capacity from that typical of a solid to that of a liquid is qualitatively similar to the findings of Greywall and Busch for the heat capacity of $^3$He on silver. Even the numerical value of their constant heat capacity is very close to our low-temperature values for $^3$He on Vycor.

We believe that the heat capacities of thin $^3$He films on silver powder and Vycor are so similar because these substrates are rough. Hence, in both cases the solid films are amorphous, probably possessing universal properties that do not depend strongly on the particular profile. What is the difference between thin $^3$He films on homogeneous and heterogeneous substrates? On Grafoil, depending on total coverage, there can exist (and coexist) almost perfect 2D phases (crystalline and liquid) with well-defined densities. Typical values of exchange parameters in the dense second crystalline layer are $J_{C_2}/k_B \sim 0.3$ mK and in liquid overlayers mean exchange parameters are $J_L/k_B \sim T_D \sim 200$ mK.[1,2,4] Hence, the temperature regions of magnetic ordering in solid and liquid phases are well separated (see dashed lines in Fig. 2). But in an amorphous $^3$He film on a sufficiently rough substrate the exchange parameters $J$ are distributed continuously, almost covering the interval between typical values of $J$ for homogeneous crystalline and liquid phases. For example, in amorphous $^3$He films of coverages 14.9 and 15.5 atom/nm$^2$ (Fig. 2) we have detected magnetic contributions up to $T \sim 50-100$ mK.

Liquid $^3$He in contact with fluorocarbon powder[13] and porous glass[14] was studied with NMR. For solid $^3$He layers on both substrates, in order to explain the linear frequency dependence of the relaxation time $T_1$, broad distributions of exchange parameters $J$ were suggested of the form

$$\frac{dN(J)}{d\ \ln J} = \text{const}, \tag{1}$$

ranging from $J_l/k_B \simeq 1.5$ $\mu$K,[14] to at least 5 – 9 mK.[13] Why does the distribution of $J$ have the functional form of Eq. (1)? Note that the magnetic properties of 3D crystalline $^3$He are well understood in the framework of the model of hard-core quantum particles of spin $\frac{1}{2}$ with many-particle exchanges (see Ref. 3 and references therein). Here, the exchange interaction $J$ is extremely sensitive to the interatomic distance, crystalline structure, dimensions, lattice deformation, and presence of defects. Obviously, in the amorphous film all these factors could lead to a broad distribution of $J$. In particular, due to the exponential dependence of $J$ on atomic density, a range of local densities in the film would yield a roughly uniform distribution of ln$J$. In Fig. 3 the schematic distributions of $J$ for $^3$He on Grafoil (a), a moderately rough substrate (b), and an extremely rough substrate (c) are shown.

Let us now calculate the nuclear exchange contribution to the heat capacity of an amorphous $^3$He film corresponding to case (c). If a magnetic system is homogeneous with a unique value of exchange parameter $J_0$, then at a temperature $T_c \sim J_0/k_B$ spins will order, which is indicated by a peak in the heat capacity. The entropy change due to the ordering of $\Delta N$ spins of $\frac{1}{2}$ is

$$\Delta S = \Delta N k_B \ln 2. \tag{2}$$

Let us suppose now that there is a distribution of local $T_c$ between $T_l$ and $T_h$, much wider than the heat capacity anomaly due to magnetic ordering for a homogeneous system. If $N(T)$ is an effective number of free disordered spins, the temperature dependence of the magnetic heat capacity is

$$C(T) = \frac{TdS}{dT} = k_B \ln 2 \frac{dN(T)}{d\ \ln T}. \tag{3}$$

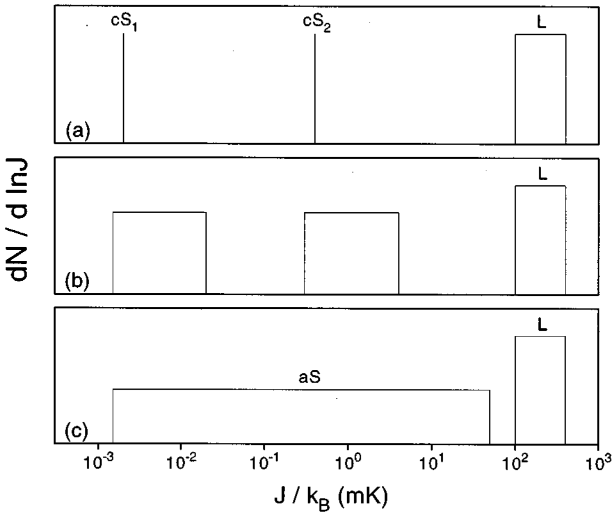

FIG. 3. Schematic representation of the density of the distribution of exchange parameter $dN/d\ \ln J$ on homogeneous (Grafoil) (a), moderately inhomogeneous (b), and extremely inhomogeneous (c) substrates (marked are the phases: $L$, liquid; $cS_1$ and $cS_2$, crystalline solid in the first and second layers; $aS$, amorphous solid).

For simplicity we will suggest that any spin ordering at some place with a local ordering temperature $T_c \sim J/k_B$ does not affect the interactions (and hence ordering temperatures) of other spins nearby. Thus, the distribution of $T_c$ is the same as the distribution of $J$ in Eq. (1):

$$\frac{dN(T)}{d\ \ln T} = \text{const}. \tag{4}$$

In this case the heat capacity [Eq. (3)] is temperature-independent,

$$C(T) = \text{const}. \tag{5}$$

If a system of $N_0$ spins orders between $T_l$ and $T_h$ having a constant heat capacity $C_0$, its value is

$$C_0 = k_B \ln 2 \frac{N_0}{\ln(T_h/T_l)}. \tag{6}$$

Let us make a numerical evaluation of $C_0$. The highest coverage studied, having no bulklike liquid contribution to the heat capacity, is 15.5 atom/nm$^2$, for which we have found a high-temperature cutoff for magnetic heat capacity $T_h \sim 100$ mK. At higher coverages some part of $^3$He atoms does not contribute to the heat capacity $C_0$, because they belong to bulklike liquid overlayers; their contribution is linear in temperature below $\sim 100$ mK and weakly affects the total heat capacity at $T \leqslant 30$ mK. A low-energy cutoff $J_l/k_B \sim 1.5$ $\mu$K for the distribution of $J$ on porous glass was reported by Kondo *et al.*[14] Thus, substituting $N_0$ = 15.5 atom/nm$^2$, $T_l = J_l/k_B = 1.5$ $\mu$K, and $T_h$ = 100 mK into Eq. (6), we get $C_0$ = 13.4 $\mu$J/K m$^2$. If there remains some low-temperature nonzero spin entropy at $T < 1$ $\mu$K, or if the real distribution of ln$T_c$ exceeds the mean constant of Eq. (4) somewhere between $T_l$ and $T_h$, the resulting experimental value of $C_0$ would be somewhat less. The result 13.4 $\mu$J/K m$^2$ is fairly close to the experimental values on Vycor and silver (Fig. 2). Namely, on silver at 15.9 atom/nm$^2$ $C$(2–7 mK) = 11.5−11.2 $\mu$J/K m$^2$; on Vycor at 15.5 atom/nm$^2$ $C$(36 mK) = 7.5 $\mu$J/K m$^2$. Again, on silver at 19.7 atom/nm$^2$ $C$(2–7 mK) = 13.2–13.0 $\mu$J/K m$^2$; on Vycor at 19 atom/nm$^2$ $C$(12–36 mK) = 8.6–10.1 $\mu$J/K m$^2$. We note that $C_0$ is only logarithmically dependent on the choice of $T_l$ and $T_h$, which are not expected to differ significantly between substrates. Thus, we can anticipate that on any rough substrate the surface heat capacity of liquid $^3$He at $T \leqslant 30$ mK will be close to this value.

There exist various disordered magnetic systems with broad distributions of exchange parameters. Randomly doped Si:P seems to be a classical example of extreme positional disorder, where each spin usually interacts with only one neighbor, the nearest one. With increasing concentration of P through the insulator-to-metal transition, the temperature dependence of the heat capacity of Si:P evolves from increasing to decreasing, being temperature-independent in between.[19] The theory of Bhatt and Lee[20] is usually employed for the interpretation of the insulating part of this heat capacity. It considers not only a wide distribution of pair exchange parameters $J$, but also a renormalization of exchange parameters of adjacent electrons after freezing out any pair of electrons in a singlet state. However, using an independently determined distribution of $J$ and neglecting any renormalization of $J$, we have succeeded in getting a value of the heat capacity of disordered $^3$He films in reasonable agreement with the experimental results. Thus, the effect of such a renormalization does not appear to be very important in our case.

Gradually increasing the $^3$He coverage [i.e., introducing new atoms with more and more extended wave functions and continuously filling the distribution of $J$ in Fig. 3(c) from left to right], we have observed an evolution from solid $^3$He with localized particles (insulator) to a Fermi liquid with delocalized quasiparticles (metal). The question appears, at which particular coverage does the insulator-to-metal transition occur, and when do the first delocalized quasiparticles appear? Sprague *et al.*[21] have studied the spin diffusion of submonolayers of $^3$He adsorbed on thin $^4$He films on Nuclepore. They have found that the low-temperature diffusion coefficient vanishes at $^4$He coverages less then 20.5 atom/nm$^2$. Presumably this indicates the proximity of such a localized-delocalized transition. If the properties of helium films on Nuclepore and Vycor are similar, we can suggest that the disappearance of the zero-temperature spin diffusion in pure $^3$He films should occur at nearly the same coverage (or perhaps higher due to enhanced mutual quasiparticle interaction). Thus, our ‘‘second statistical layer’’ of $^3$He on Vycor (19 atom/nm$^2$) could be still localized (insulating), though already having some features of bulk liquid.

To summarize, we have measured the heat capacity of $^3$He films on Vycor glass at $10 \leqslant T \leqslant 600$ mK. With increasing the coverage from 1 to 3 atomic layers, the heat capacity of disordered $^3$He films evolves from that typical to solid to that of liquid $^3$He, being weakly temperature dependent at thicknesses of about two layers. A model is proposed for the magnetic origin of the heat capacity of this intermediate layer, using a wide uniform distribution of the logarithm of exchange parameters suggested from NMR study of $^3$He on disordered substrates. It yields the value of about 13 $\mu$J/K m$^2$, which is close to the experimental results for $^3$He on silver and Vycor. We explain this ‘‘anomalous heat capacity’’ in terms of gradual spin ordering in a random magnet. In this framework, the results of the calorimetric study of $^3$He on rough substrates (ours and from Ref. 5) are consistent and complementary with the results of NMR investigations.[13,14]

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*On leave from the Institute of Solid State Physics, Russ. Acad. Sci., Chernogolovka 142432 Moscow prov., Russia. Present address: Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo-106, Japan.

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