Evidence of 1D behaviour of He\textsuperscript{4} confined within carbon-nanotube bundles

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We present the first low-temperature thermodynamic investigation of the controlled physisorption of He\textsuperscript{4} gas in carbon single-wall nanotube (SWNT) samples. The vibrational specific heat measured between 100 mK and 6 K demonstrates an extreme sensitivity to outgassing conditions. For bundles with a few number of NTs the extra contribution to the specific heat, $C_{ads}$, originating from adsorbed He\textsuperscript{4} at very low density displays 1D behavior, typical for He atoms localized within linear channels as grooves and interstitials, for the first time evidenced. For larger bundles, $C_{ads}$ recovers the 2D behaviour akin to the case of He\textsuperscript{4} films on planar substrates (grafoil).

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The discovery of carbon nanotubes is very exciting from the academic point of view, but also for engineering purposes. Reducing dimensionality can bring entirely new properties for the thermodynamics of vibrational states for nanotubes as well as for the mechanisms of gas adsorption (in structures like bundles), in particular He\textsuperscript{4}, which has already been largely investigated in the 2D case. 1D confinement of vibrational modes was supposed to explain the specific heat ($C_p$) in SWNT measured down to 2 K \cite{1}. He within the interstitials in nanotube bundles was expected to condense into a lattice gas \cite{2}. Our recent $C_p$ measurements did not support these both expectations \cite{3}; but they yielded $C_p$ results of pristine nanotubes and showed a remarkable influence of a relatively small quantity of adsorbed He, which in particular allows the comparison to the case of He films in 2D configurations, already largely investigated \cite{4,5,6}.

In this Letter we present the low-T specific heat investigation on two SWNT samples in similar conditions as far as adsorbed He\textsuperscript{4} is concerned. The first sample was prepared by laser vaporization (sample LV) and the second one by electric-arc discharge (sample AD). X-ray and neutron diffraction, and Raman experiments were systematically used for the characterization of both samples \cite{7,8}.

Sample LV (synthesized in “Rice University conditions” \cite{9}) was obtained by laser vaporization at 1100°C with Ni and Co catalysts, up to at. 2% as residual concentration in final samples. The SWNTs of mean diameter 1.4 nm, with a standard deviation of 0.2 nm \cite{7} form bundles organized in the usual hexagonal lattice of parameter 1.7 nm. Bundles with a diameter of 10-13 nm contain typically 30-50 tubes, with an extension up to 20 nm (i.e. up to $N_t \sim$100 tubes). The LV sample (m=45 mg) in form of several elastic foils (buckypaper as in ref. \cite{10}) was used for previous heat capacity measurement \cite{3}. Sample AD was synthesized at Montpellier by arc-discharge \cite{10}, with Ni (0.5%) and Y catalysts (0.5%), in total 1 at. %, and with no Co. The individual SWNT of similar diameter as in sample LV \cite{7,8} here are organized in bundles generally smaller in diameter – up to 10 nm with $N_t$ less than 20-30 tubes. The AD sample (m=90 mg) was in a form of pellet (13 mm in diameter, 1 mm thick) obtained by pressurisation of powder with 10 kbar \cite{11}. Within the usual purification technique, the nanotubes are close-ended. So, we suppose that no adsorption can occur within the tubes, and only interstitials or external grooves and surfaces of the bundles are the most probable occupancy sites. Both samples were mounted in the same manner \cite{8} in a glove box under nitrogen atmosphere to avoid at maximum gaseous contamination from ambient air and thereafter transferred in the dilution cryostat. The data were collected by the transient heat pulse method between 100 mK and 6 K.

We have studied the adsorption in LV and AD samples by simply using our usual cooling procedure down to 4.2 K, He\textsuperscript{4} being the exchange gas \cite{8}. After initial pumping at room temperature, He\textsuperscript{4} is introduced in the calorimeter chamber at 77 K at a pressure of 6-7 $10^{-2}$ mbar. Normally, when the sample does not adsorb, at 4.2 K we pump out the exchange gas in order to get good conditions for $C_p$ measurements ($\sim$10$^{-6}$ mbar). Spectacularly, in LV samples all the He\textsuperscript{4} was adsorbed, so that cooling down to He temperature was not possible without a new injection! This was the first evidence of the strong He adsorption in SWNT samples. As it is well-established that He\textsuperscript{4} is totally desorbed by reheating up to 25-30 K \cite{1,3,12}, we used this procedure to obtain the first desorbed state - run A \cite{8}. In addition, a further long secondary pumping (a few days to a whole week) at 300 K, coupled with the above very efficient desorbing procedure (reheating from 4.2 to 40 K) was used to define the heat capacity in the best outgassing conditions (run C for LV sample \cite{8} and III in AD sample).
Figure 1 presents the new data collected on the AD sample. State I was obtained with the usual He dose for cooling the sample down to 4.2 K and successive pumping under secondary vacuum at 5 K. State II corresponds to more efficient outgassing conditions - reheating under active pumping up to 15 K. As this temperature is too low for a complete desorption, this run represents a case of intermediate He adsorption. The most efficient desorption procedure was performed for State III (equivalent of run C for LV in Ref. [3]). First the sample was under active secondary pumping during one week at 300 K. After it was cooled down to 4.2 K (following procedure I). Finally, further reheating to 35-40 K enabled complete outgassing of He. Consequently, we take $C_p$ of State III as the pristine nanotube value, corresponding to the vibrational contribution. Here we only indicate that the extrinsic contribution of the ferromagnetic catalyst, which shows up via a nuclear hyperfine term $C_N$, is much smaller than in LV sample due to the absence of Co [13]. This term is subtracted and below 0.15 K, was much smaller than in LV sample due to the extrinsic contribution of the ferromagnetic catalyst, which is consistent with a smaller number of tubes $N_t$ in the bundle. This softening of the inter-tube cohesive forces - decrease of transverse sound velocity - is also in agreement with the larger $\beta$: being $0.072 \text{ mJ/gK}^4$ in AD compared to $0.035 \text{ mJ/gK}^4$ in LV [3].

To go further with the analysis, we make the assumption that the contribution of adatoms to the specific heat is additional to that of the pristine SWNT. It holds to a great accuracy due to the fact that the adsorbate modes couple only weakly to the substrate vibrational modes (the substrate atomic mass mismatch is large - 4/12). Hence we obtain $C_{ads}$ after subtracting the corresponding pristine values; run C for LV [3] and state III for AD. $C_{ads}$ for the maximum adsorption is presented in Figure 2 and for the case of intermediate adsorption in Figure 3.

Here we repeat that the pressure of He gas admitted in the sample chamber was the same in both cases (corresponding to $N_0=7 \times 10^{13}$ atoms). However the AD sample having two times larger mass, the maximal number of accessible He atoms per one C atom was 3% in LV sample and 1.5% in the AD sample; this fact together with the different sample topologies (characterized with $N_t$) will be crucial in our interpretation of $C_{ads}$.

$C_{ads}$ represents at least 50% of the total $C_p$ (at 1 K) in our conditions. It exhibits a striking similarity for both samples which certainly reflects the same thermo-
in the plateau region should indicate the effective dimen-
sionality for the He atomic excitations, being \(0.5 \, k_B\) for a 1D gas or \(1 \, k_B\) for a 2D fluid (gas or liquid). The rise of the plateau over \(1 \, k_B\) corresponds to the occupation of excited single-particle states in the direction perpendicular to the surface, i.e. announcing the 3D ordering (as the completion of the first 2D monolayer).

For the intermediate adsorption state (Figure 3) there is again a similar qualitative behaviour for both systems; after an initial increase, there is a saturation towards a plateau which extends from 1.5 to 5 K for AD or from 3 K to 5 K for LV sample. The value of \(C_{ads}\) per He atom in the plateau region should indicate the effective dimensionality for the He atomic excitations, being \(0.5 \, k_B\) for a 1D gas or \(1 \, k_B\) for a 2D fluid (gas or liquid). The rise of the plateau over \(1 \, k_B\) corresponds to the occupation of excited single-particle states in the direction perpendicular to the surface, i.e. announcing the 3D ordering (as the completion of the first 2D monolayer).

For the estimation of the corresponding number of He adatoms in the partially outgassed states (Figure 3) for each sample, we have used informations from the desorption experiments, which were performed in quite similar conditions as here [12, 16]. For two outgassing conditions corresponding to different desorption temperatures, \(T_D \sim 15\) K for AD and 25-30 K for LV sample, the remaining numbers of He atoms were estimated as \(N_{AD} \sim N_0/10\) and \(N_{LV} \sim N_0/20\), i.e. \(N_{AD} \sim 7 \times 10^{18}\) and \(N_{LV} \sim 3.5 \times 10^{18}\) [17]. Consequently, using absolute values of \(C_{ads}\) given in the inset of Figure 3, 38 \(\mu J/K\) for AD (90 mg) and 45 \(\mu J/K\) for LV (45 mg) – the corresponding plateau values per one He atom are 0.4 \(k_B\) for AD and 0.95-1.0 \(k_B\) for LV.

It is very difficult to reconcile these extreme cases (2D-LV behavior and 1D-AD behavior) if one only considers the absolute number of He adatoms, \(N_{AD} > N_{LV}\), which seems to lead to the inverse effect! In fact, contrary to the case of He films on planar substrates where the He behavior is surprisingly independent of the structure of the substrate [5], here we are in the case where the topology of the substrate plays an essential role. This appears to be a natural conclusion in the case of C-nanotube bundles. That finally gives the opportunity to detect 1D effects in confined He (in a very diluted limit), which was not possible (or evidenced) in low-T He films.

The essential topological difference between AD and LV samples is the main size of the bundles [7, 8]. In order to make the most simple analysis, we neglect the certain distribution in size and we suppose that AD bundles have 19 tubes and LV 61 (corresponding to 3 or 5 tubes on each facet in regular hexagonal arrays). There are three specific sites of adsorption for He [19]: interstitials (IC), outer grooves (G) and bundle surface (S). Recent adsorption isotherm measurements [20], consistent with He desorption experiments [12, 11], indicate that adsorption is first in the outer grooves of the bundles, then filling the rest of the outer surface, and finally layering on the outer surface (in successive layers). Monte-Carlo simulations [21] show an extreme pressure sensitivity and an abrupt crossover from 2D coverages to 1D filling, which successively leaves G and IC channels as the last refuge for the He atoms on progressive lowering pressure. From the above \(N_{AD}\) and \(N_{LV}\) values, we now estimate, using these topological considerations, the possible occupied places, either in outer 2D graphene surfaces or 1D (IC and G) channels.

For this purpose, we make the following assumptions: we start from an effective adsorption surface of \(\sim 300\) \(\text{m}^2/\text{g}\) per nanotube, in good correspondence with 80 \(\text{m}^2/\text{g}\) for a typical bundle of \(N_s=37\) [20]. Now we suppose that a complete coverage of external surfaces (2D sites) varies between 12 and 9 He sites (between 2 grooves on facets) for AD and LV (\(N_s=19\) and 61 respectively). Taking also into account the possible adsorption in the 1D channels (G + IC), this yields \(S_{eff}=100\) \(\text{m}^2/\text{g}\) for \(N_s=19\), and \(70\) \(\text{m}^2/\text{g}\) for \(N_s=61\), with 80% and 66% of sites in surface, respectively. For our sample masses, we get 2.0 \(\text{m}^2\) of effective surfaces for 1D channels and 7.0 \(\text{m}^2\) for external surface in AD sample, and 1 \(\text{m}^2\) for 1D and 2.0 \(\text{m}^2\) for surface of LV sample. We suppose that adsorption takes place in the same external conditions (i.e. supposing similar binding potentials) and that 12 atoms/\(\text{m}^2\) is a complete layer coverage, as for He-films. Consequently, the final configurations for the total desorption of \(N_0\) atoms of He at \(T=4\) K should be for AD sample: all 1D channels occupied and around 1/2 of the outer...
surface of bundles and for LV sample: all 1D channels, 2 external layers occupied, and 50% of a third layer.

Outgassing starts from the outer surfaces and continues with atoms at the lower surfaces. In the case of AD sample ($T_D=15$ K and remaining $N_{AD} \sim 7 \times 10^{18}$), first all He atoms of the surface ($\sim 5 \times 10^{15}$) were degassed [10, 21]. Further degassing empties the groove regions [22] and probably also some weakly bond IC sites (in total $0.7 \times 10^{19}$) [21]. Finally, He remains only in some IC sites [21, 22], i.e., about 50% of the IC sites are still occupied. This is the origin of 1D He confinement behaviour in AD as demonstrated in Figure 3. Also consistent with our 1D interpretation for the AD sample is the very rapid decrease of the He heat capacity below 1 K, which can be well fitted with an Einstein function, varying like $(\Theta_E/T)^2 \exp(-\Theta_E/T)$, with $\Theta_E=3.8$ K (Figure 3). This indicates independent harmonic oscillators, probably localized. At our knowledge, the exponential decay has never been observed in He on grafoil. It was supposed to occur at very low coverage, i.e., with a very feeble $C_p$ signal [4, 5].

For the LV sample, outgassing is of a higher cost in energy because one has to outgass the successive layers and the corresponding desorption energy should be much larger for completely removing the 1st layer [21]. The heat of adsorption of the second layer for He on grafoil is very large (35 K) in comparison to the third (15 K) and the following [4]. We conclude that, even at a desorption temperature of 25-30 K, there remains still a considerable number of 2D He coverages for this sample. This is consistent with the 2D behaviour of $C_{ads}$, which clearly shows a quadratic regime over more than one decade in $T$: $C_{ads} = 2.7-2.8 T^2$ mJ/g K (Figure 3). This is signature of a 2D–fluid or solid-regime for adsorbed He. For the fluid case, consistent with the limit $C/R \to 1$ (R is the gas constant), for the molar heat capacity of He, the corresponding 2D Debye temperature for only longitudinal phonons is: $C_{ph} = 14.42 R (T/\Theta)^2$ [23], so that $C_{ads} = 2.1 T^2$ J/molK yields $\Theta = 7.5$ K. This value can be compared to 5.1 K obtained in the same $T$-range (0.1-0.5 K) for the first layer of He on grafoil [4]. In addition, the amplitude of the $T^2$ regime (or the Debye $T$) is rather independent of the order of the layer up to the third one [4].

In conclusion, we gave the first thermodynamical evidence of 1D confinement of He in NT bundles, as well as 2D behavior of $C_{ads}$ for bundles with larger size. These results suggest further studies of the crossover between 1D to 2D adsorbate behavior by varying, for a given topology of the NT bundles, the concentration of He atoms in the dilute limit. This is of great significance, since it may give basic informations on the very low energy states of He, such as zero-point energy, localization, etc /dots. The remarkable absence of peaks of $C_{ads}$ in this $T$ range indicates a strong influence of size-effects imposed by NT bundles compared to conventional He films, such as on grafoil. This could be accounted for by a much shorter correlation length which inhibits the development of structural phase transitions. One result which remains to be explained is $C_{ads} \sim T^{1.1}$ for rather large adsorption levels (a few at.% of He, when the adsorbate behavior is essentially determined by the external “dressing” of the bundles). This seems to be a completely new physics in comparison to the previous results obtained for the successive layering processes on purely 2D substrates like grafoil and deserves some theoretical considerations.

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