Supplementary Information Layering transition in superfluid helium adsorbed on a carbon nanotube mechanical resonator

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I. QUANTUM ELECTRON TRANSPORT MEASUREMENTS

Figure 1a shows that the electrical characteristics of the nanotube studied in this work is typical of ultraclean nanotubes [1]. Near $V_{\rm G}^{\rm DC} = 0$ V, the conductance is suppressed to zero due to the small energy gap of the nanotube [2]. For positive $V_{\rm G}^{\rm DC}$ values, p-n junctions are formed near the metal electrodes. It creates Coulomb blockade peaks in the conductance (Fig. 1b). For negative $V_{\rm G}^{\rm DC}$, the nanotube is *p*-doped along the whole tube, resulting in a larger conductance approaching the quantum conductance $4e^2/h$ of small-gap nanotubes. In this regime, the conductance is modulated due to quantum electron interference [3]. Here, *e* is the charge of the electron and *h* is the Planck constant.

Figure 1c demonstrates that the nanotube is of high quality, since the modulation of the conductance is periodic over a large range of $V_{\rm G}^{\rm DC}$, and since this periodic modulation due to electron interference would be deteriorated by a tiny amount of disorder.

We quantify the nanotube length $L = 1.1 \ \mu \text{m}$ from the characteristic voltage bias $V_{\text{C}} = 1.5 \text{ mV}$ of the electron interference pattern shown in Fig. 1c using $L = hv_{\text{F}}/2eV_{\text{C}}$ [3]. Here, $v_{\text{F}} = 8 \times 10^5 \text{ m/s}$ is the Fermi velocity of nanotubes. This length is consistent with the width of the trench. We also obtain a similar length from the Coulomb blockade measurements in Fig. 1b. From the separation $\Delta V_{\text{G}}^{\text{DC}} = 18 \text{ mV}$ between two conductance peaks, we obtain the nanotube-gate capacitance $C_{\text{G}} = e/\Delta V_{\text{G}}^{\text{DC}} = 8.9 \times 10^{-18} \text{ F}$. We get the length $L \simeq 1 \ \mu \text{m}$ of the suspended nanotube using

$$C_{\rm G} = \frac{2\pi\epsilon_0 L}{\ln\left(\frac{2d}{r}\right)},\tag{1}$$

where ϵ_0 is the vacuum permittivity, d = 350 nm the separation between the nanotube and the gate electrode, and r the nanotube radius. This estimation of the length is less reliable than the previous one because Eq. 1 does not take into account the screening of the electric



FIG. 1. Electron transport measurements of the nanotube discussed in the main text. (a,b) Conductance of the nanotube as a function of gate voltage measured at the base temperature of the cryostat over two different gate voltage ranges. (c) Differential conductance as a function of $V_{\rm SD}^{\rm DC}$ and $V_{\rm G}^{\rm DC}$ at the base temperature of the cryostat. The intersection of the white lines at $V_{\rm C} = 1.5$ mV corresponds to the characteristic voltage bias of the electron interference

field between the nanotube and the gate electrode by the source and the drain electrodes.

II. TRANSDUCTION OF DISPLACEMENT INTO CURRENT

We measure the mechanical vibrations of the nanotube with the two-source technique [4, 5]. Displacement modulations result in current modulations by applying an input oscillating



FIG. 2. Variance of the mechanical displacement as a function of temperature. Measurements are carried out on the nanotube discussed in the main text.

voltage with amplitude $V_{\rm SD}^{\rm AC}$ across the nanotube. We assume that the resonance used in the measurements of the main text corresponds to the fundamental eigenmode polarized in the direction perpendicular to the surface of the gate electrode, which is a good assumption since the signal of the driven vibrations of this resonance is much larger than the signal of the other resonances. The current δI at the frequency close to the difference between the mode eigenfrequency and the frequency of the source-drain voltage is

$$\delta I = \beta \delta z,\tag{2}$$

$$\beta = \frac{1}{2} \frac{dG}{dV_{\rm G}} V_{\rm G}^{\rm DC} V_{\rm SD}^{\rm AC} \frac{C_{\rm G}'}{C_{\rm G}}.$$
(3)

Here, δz is the displacement of the nanotube, $dG/dV_{\rm G}$ is the derivative of the conductance with respect to the gate voltage, $V_{\rm G}^{\rm DC}$ is the static gate voltage, and $C'_{\rm G}$ is the derivative of $C_{\rm G}$ with respect to z. We quantify $C'_{\rm G} = 4.1 \times 10^{-12}$ F/m using the relation $C'_{\rm G} = \frac{C_{\rm G}}{d\ln(2d/r)}$.

We estimate the effective mass m = 3.5 ag from the measurement of the variance of the displacement noise $\langle \delta z^2 \rangle$ as a function of temperature T (Fig. 2). The displacement noise of the nanotube is measured with the electrical method described in Ref. [5] and using Eqs. 2 and 3. We compare the measured slope of $\langle \delta z^2 \rangle$ as a function of T to the slope expected

from the equipartition theorem, which reads $m\omega_0^2 \langle \delta z^2 \rangle = k_b T$. Here, $\omega_0/2\pi$ is the resonance frequency of the eigenmode and k_b is the Boltzmann constant. This mass is consistent with the mass of a ~ 1.1 µm long nanotube.

We evaluate the nanotube radius $r \simeq 1.5$ nm from the effective mass using the relation

$$m = \frac{1}{2} \left(2m_{\rm C} \times \frac{2\pi r \times L}{A_{\rm h}} \right),\tag{4}$$

where $m_{\rm C} = 2 \times 10^{-26}$ kg is the mass of a carbon atom and $A_{\rm h} = 5.2 \times 10^{-20}$ m² is the surface area of a hexagon in the honeycomb lattice of graphene. The coefficient $\frac{1}{2}$ on the right-hand side of Eq. 4 comes from the normalisation of the mass of the resonator due to the shape of the eigenmode. We assume here that the modal shape is $\phi(x) = \cos(\pi x/L)$, a good approximation for the shape of a beam under tension.

III. DENSITY OF HELIUM LAYERS

We can reliably quantify the ratio between the number N_{He} of adsorbed helium atoms and the number N_{C} of carbon atoms at the surface of the nanotube from the measurement of the resonance frequency [6, 7]. This ratio, called coverage, reads

$$\phi = \frac{N_{\rm He}}{N_{\rm C}} = \frac{m_{\rm C}}{m_{\rm He}} \left[\left(\frac{f_0^{\rm NT}}{f_0^{\rm NT+He}} \right)^2 - 1 \right],\tag{5}$$

where $m_{\rm C}$ and $m_{\rm He}$ are the atomic masses of carbon and helium atoms, respectively. Here, $f_0^{\rm NT+He}$ is the resonance frequency of the nanotube covered by helium atoms, and $f_0^{\rm NT}$ is

		Areal density $(atoms/nm^2)$	
	$f_0 (MHz)$	nanotube	graphite
Pristine substrate	36.34	0	0
First layer completed	34.41	11.0	11.4
Second layer completed	32.97	8.1	8.6
Third layer completed	31.69	7.2	7.6
Fourth layer completed	30.39	7.3	7.6

TABLE I. Areal density of completed helium layers on the nanotube. The density of helium adsorbed on graphite is also shown [8].

the resonance frequency of the pristine nanotube without any adsorbed helium atoms. The coverage of noble gas atoms adsorbed on nanotube resonators can be successfully quantified with Eq. 5 because these adsorbed atoms increase the mass of the resonator but do not modify its spring constant [6, 7]. Indeed, the interaction between noble gas atoms is much weaker than that between the carbon atoms of the nanotube.

Table I shows the areal density of the different completed helium layers. The areal density is estimated from the coverage and taking into account the cylindrical geometry that normalizes the density by the factor $\frac{r}{r+i\cdot d_1}$. Here, r is the nanotube radius, i is the layer number, and d_1 is the layer-layer separation. The characterisation of the nanotube in the previous section indicates that r = 1.5 nm. The separation between layers is taken equal to $d_1 = 0.27$ nm, the separation between the first helium layer and graphite [9]. Table I shows that the estimated areal densities are remarkably close to the values measured with helium adsorbed on graphite [8].

IV. RESONANCE FREQUENCY SHIFT – A MASS EFFECT OR A SPRING EFFECT?

We look at the f_0 dependence of two different frequency shifts, namely Δf_0 and δf_0 (see Fig. 2 in the article), which show opposite behavior. The resonance frequency of the nanotube covered by helium depends on three parameters: the helium pressure in the cell P_{He} , the temperature T, and the gate voltage V_{G}^{DC} . The resonance frequency of the bare nanotube depends only on the DC gate voltage V_{G}^{DC} as

$$f_0(V_{\rm G}^{\rm DC}) = \frac{1}{2\pi} \sqrt{\frac{k_{\rm NT}(V_{\rm G}^{\rm DC})}{m_{\rm NT}}},$$
 (6)

where the nanotube stiffness $k_{\rm NT}$ can be changed by tuning the gate-voltage $V_{\rm G}^{\rm DC}$, in contrast to the nanotube mass $m_{\rm NT}$. We measure that $f_0(V_{\rm G}^{\rm DC})$ is temperature independent at a fixed $V_{\rm G}^{\rm DC}$. Straining the nanotube with gate voltage is very efficient, since $f_0(V_{\rm G}^{\rm DC})$ can be varied by ~ 16% in Figs. 2b and 2d of the article. Due to the large nanotube stiffness, the longitudinal deformation of the nanotube is minute and the helium film structure also. Furthermore, the surface density of helium on the nanotube is fixed by the temperature and the helium pressure in the cell. The resonance frequency of the nanotube coated by a thin helium film is:

$$f_1 = \frac{1}{2\pi} \sqrt{\frac{k_{NT} + k_{He}}{m_{NT} + m_{He}}} \approx f_0 \left(1 - \frac{m_{He}}{2m_{NT}} + \frac{k_{He}}{2k_{NT}}\right)$$
(7)

High-frequency nanotube mechanical resonators are highly sensitive to helium coating. Loading the nanotube with a single helium layer gives rise to a mass increment $m_{\rm He}/m_{\rm NT} \lesssim 10\%$ and a decrease of the resonance frequency $(f_1 - f_0)/f_0 \approx -m_{\rm He}/2m_{\rm NT} \lesssim -5\%$. A second effect of the helium coverage is the modification of the nanotube spring constant due to a modification of the surface tension. The effect is extremely small because of the weak He-He interaction compared to the covalent C-C interaction, but still measurable thanks to the remarkable sensitivity of high-Q nanotube resonators. By studying the $V_{\rm G}^{\rm DC}$ dependence of the frequency shifts, it is possible to distinguish the two contributions. Indeed, as a function of the helium pressure and the temperature, the frequency shift is expressed as

$$f_0 - f_1 \approx f_0(V_{\rm G}^{\rm DC}) \left(\frac{m_{\rm He}(P_{\rm He}, T)}{2m_{\rm NT}} - \frac{k_{\rm He}(P_{\rm He}, T)}{2k_{NT}(V_{\rm G}^{\rm DC})} \right),$$
 (8)

$$f_0 - f_1 \approx \left(\frac{1}{2m_{\rm NT}}\right) \left(f_0(V_{\rm G}^{\rm DC}) \times m_{\rm He}(P_{\rm He}, T) - \frac{k_{\rm He}(P_{\rm He}, T)}{4\pi^2 f_0(V_{\rm G}^{\rm DC})}\right).$$
 (9)

Mass effects increase proportionally to f_0 whereas stiffness effects decrease proportionally to $(1/f_0)$. The former depends on the adsorbed helium mass, consequently on the gas pressure, on temperature, possibly also on changes in superfluid mass fraction. The later addresses the physics of the helium surface tension which carries additional signatures of the layering transition. Note that a $V_{\rm G}^{\rm DC}$ -dependence of $k_{\rm He}$ and $m_{\rm He}$ would intervene as a second order correction in the developments, which justifies the above variable separation.

Let us now look at the f_0 dependence of the frequency shift Δf_0 that is indicated on Fig. 2c of the article. We expect it to be a mass effect due to the helium evaporation between 10 mK and 10K so that Δf_0 should obey the equation:

$$\Delta f_0 \approx \frac{f_0 (V_{\rm G}^{\rm DC}) m_{\rm He} (P_{\rm He}, 10 \text{ mK})}{2m_{\rm NT}}.$$
 (10)

 Δf_0 should be an increasing function of f_0 , in agreement with the measurements on Fig. 2b of the article.

On the opposite, Fig. 2d of the article shows that δf_0 is a decreasing function of f_0 which demonstrates that this slight frequency dip is due to some change in the elastic constant k_{He} . Indeed it writes now:

$$\delta f_0 \approx -\frac{\delta k_{\rm He}(P_{\rm He})}{8\pi^2 m_{\rm NT} f_0(V_{\rm G}^{\rm DC})} \tag{11}$$

where δk_{He} is the change in the helium surface tension from 10 mK to the temperature of the minimum (about 0.5K, see Fig. 2c of the article). Here, δk_{He} is negative and we attribute it to the increasing entropy of the helium film. In this case, one expects that δf_0 decreases with f_0 , which is confirmed by our measurements (see Fig. 2d of the article). We cannot attribute it to some superfluid-normal transition in the film because this would be a mass effect with the opposite dependence on f_0 . As shown in the next section, we have calculated the temperature dependence of the helium surface tension, which can describe our measurements.

V. SURFACE TENSION – THERMALLY EXCITED THIRD SOUND STATES

We show in the main text that the measured spring constant of the nanotube covered by superfluid helium is temperature dependent. In this section, we relate this observation to the change of the surface tension of the superfluid due to thermally excited third sound states.

The surface tension γ is the free energy of the superfluid surface per unit area. When varying the superfluid surface area by δA , the energy changes as

$$\delta E = \gamma \cdot \delta A. \tag{12}$$

The surface tension contributes to the spring constant of the resonator. Any small deviation from the equilibrium position of the superfluid leads to a spring force. The modulation δA is related to the modulation of the resonator length δl when the nanotube is vibrating. The modulation is $\delta A = 2\pi r_{\text{He}} \cdot \delta l$ where r_{He} is the radius of the surface of the helium superfluid covering the nanotube. In order to relate δl to the displacement δz of the nanotube resonator, we consider the fundamental mode of a doubly-clamped nanotube string. The transverse displacement of the resonator along its axis x is given by $Z(x,t) = \delta z(t) \cdot \phi(x) =$ $\delta z(t) \cdot \cos(\pi x/L)$ with $\phi(\pm L/2) = 0$ the boundary conditions at the clamping points. When the nanotube moves by δz , the total length becomes

$$L + \delta l = \int_{-L/2}^{+L/2} dx \sqrt{1 + \left(\frac{\partial Z}{\partial x}\right)^2} \simeq L + \frac{1}{2} \int_{-L/2}^{+L/2} dx \left(\frac{\partial Z}{\partial x}\right)^2 = L + \frac{\pi^2}{4L} \delta z^2.$$
(13)

As a result, the energy associated to the surface tension of the superfluid film is the energy

of a harmonic oscillator $\delta E = \frac{1}{2}k_{\text{He}}\delta z^2$ with spring constant

$$k_{\rm He} = \gamma \pi^3 \frac{r_{\rm He}}{L}.$$
 (14)

The restoring force of the helium film acts in parallel to the restoring force of the pristine carbon nanotube $k_{\rm NT}$, so that the total spring constant is $k_{\rm total} = k_{\rm He} + k_{\rm NT}$. It is important to emphasize that the helium film contributes weakly to the total spring constant, since the interaction between noble gas atoms is 2 orders of magnitude weaker than that of covalent C-C bonds, as demonstrated experimentally in Refs. [6, 7]. For this reason, any change of the surface tension leads to a minuscule change of the resonance frequency of the resonator, as observed in our experiments discussed in the main text.

It is interesting to compare the typical elongation δl in our experiments with the separation between two helium atoms. The modulation of the elongation is small so that the number of helium atoms adsorbed on the suspended nanotube remains constant. Indeed, the amplitude of the thermal vibrations is ≤ 300 pm below T = 1 K so that the associated nanotube elongation is $\delta l \leq 0.2$ pm using Eq. 13. For comparison, the separation between helium atoms in thin films is typically 0.3 nm.

The temperature dependence of the surface tension arises from the change of the free energy of the superfluid, that is, from the thermal excitation of two-dimensional third sound states. To compute $\gamma(T)$, we follow the calculations of Atkins using third sound states instead of the surface tension waves in three-dimensional superfluid helium [10]. Below 1 K, the third sound dispersion is given by

$$\omega = ck \tag{15}$$

with the angular frequency ω , the superfluid velocity c, and the wavevector strength k [11]. In order to calculate the density of states, we first count the number $N_{\rm st}$ of states within the surface πk^2

$$N_{\rm st} = \frac{L_0^2}{(2\pi)^2} \pi k^2 \tag{16}$$

with L_0^2 the surface area. The density of states is given by the number of states within the frequency $\delta\omega$ and per unit of surface,

$$\frac{g(\omega)\delta\omega}{L_0^2} = \frac{1}{L_0^2}\delta N_{\rm st} = \frac{1}{L_0^2}\frac{dN_{\rm st}}{dk}(\frac{d\omega}{dk})^{-1}\delta\omega = \frac{\omega}{2\pi c^2}\delta\omega$$
(17)

The internal energy of thermally excited third wave states per unit surface is then

$$U_{\rm th} = \int_0^\infty \frac{\hbar\omega}{\exp(\hbar\omega/k_{\rm B}T) - 1} g(\omega) d\omega = \frac{1}{2\pi c^2} \frac{(k_{\rm B}T)^3}{\hbar^2} \int_0^\infty \frac{x^2}{\exp(x) - 1} dx = 0.38 \frac{(k_{\rm B}T)^3}{(\hbar c)^2}.$$
 (18)

When the internal energy varies as $U \propto T^{\lambda}$, the free energy scales as $F = -\frac{1}{\lambda-1}U$ from simple thermodynamics [10]. As a result, the variation of the free energy per unit surface when increasing the temperature from 0 K is

$$\Delta\gamma(T) = U_{\rm th} - TS = -\frac{1}{2}U_{\rm th}.$$
(19)

Here, S is the entropy per unit surface. As a result, we obtain

$$\Delta\gamma(T) = -0.19 \frac{(k_{\rm B}T)^3}{(\hbar c)^2}.$$
(20)

The change in free energy is related to the change in spring constant using Eq. 14

$$\delta k_{\rm He}(T) = -5.89 \frac{r_{\rm He}}{L} \frac{(k_{\rm B}T)^3}{(\hbar c)^2},\tag{21}$$

When increasing the temperature from 0 K, the resonance frequency f_0 of the nanotube string covered by the helium film is expected to decrease as

$$\delta f_0(T) = \frac{1}{2} \frac{\delta k_{\rm He}(T)}{k_{\rm NT}} f_0 = -0.074 \frac{1}{m_{\rm NT} f_0} \frac{r_{\rm He}}{L} \frac{(k_{\rm B}T)^3}{(\hbar c)^2}.$$
 (22)

VI. THEORETICAL CALCULATIONS

Figures 3a,b show the energy per ⁴He atom as a function of density for the first and second layer, respectively. Calculations are performed using diffusion Monte Carlo method, as described in ref [12]. The calculations are performed for a nanotube radius of 1.43 nm.

On Fig. 3a is displayed the energy of atoms in both a liquid (red) and solid (blue) configuration when the nanotube is covered by one layer. The ground state of the system corresponds to a liquid of density $0.0432 \pm 0.003 \text{ Å}^{-2}$. From a density of $0.087 \pm 0.005 \text{ Å}^{-2}$ up, the solid structure is more stable than the liquid. We then conclude that at the second layer promotion (density of $\approx 0.12 \text{ Å}^{-2}$) the first layer is solid. This is consistent with measurements and calculations on helium adsorbed on graphite [8, 13].

On Fig. 3b is displayed the energy of the atoms in the second layer. The ground state of the system always corresponds to a liquid. The result of these calculations is different



FIG. 3. Calculated energy per atom in the first layer and the second layer (a) First layer. (b) Second layer. Energy per atom for both a liquid (red circles) and a solid (blue squares).

from that of previous works on helium adsorbed on graphite, where the second layer at completion is solid [8, 13]. More work has to be carried out in order to be able to make a firm conclusion on the phase of the second layer adsorbed on nanotubes. For this, a more advanced model can be used in order to take into account for instance the corrugation of the nanotube.

- J. Moser, A. Eichler, J. Güttinger, M. I. Dykman, A. Bachtold, Nature Nanotech. 9, 1007 (2014).
- [2] E. A. Laird, F. Kuemmeth, G. A. Steele, K. Grove-Rasmussen, J. Nygard, K. Flensberg, L.
 P. Kouwenhoven, *Rev. Mod. Phys.* 87, 703 (2015).
- [3] W. Liang, M. Bockrath, D. Bozovic, J. H. Hafner, M. Tinkham, H. Park, *Nature* **411**, 665 (2001).
- [4] V. Sazonova, Y. Yaish, D. Üstünel, D. Roundy, T. A. Arias, P. L. McEuen, *Nature* 431, 284 (2004).
- [5] S. L. de Bonis, C. Urgell, W. Yang, C. Samanta, A. Noury, J. Vergara-Cruz, Q. Dong, Y. Jin,
 Y., A. Bachtold, *Nano Lett.*, 18, 5324 (2018).
- [6] Z. Wang, J. Wei, P. Morse, J. G. Dash, O. E. Vilches, D. H. Cobden, Science, 327, 552 (2010).
- [7] A. Tavernarakis, J. Chaste, A. Eichler, G. Ceballos, M. C. Gordillo, J. Boronat, A. Bachtold, *Phys. Rev. Lett.*, **112**, 196103 (2014).
- [8] P. A. Crowell, J. D. Reppy, *Phys. Rev. B*, **53**, 2701 (1996).
- [9] P. Corboz, M. Boninsegni, L. Pollet, M. Troyer, Phys. Rev. B, 78, 245414 (2008).
- [10] K. R. Atkins, Can. J. Phys., **31**, 1165 (1953).
- [11] J. E. Rutledge, W. L. McMillan, J. M. Mochel, T. E. Washburn, *Phys. Rev. B*, 18, 2155 (1978).
- [12] M. C. Gordillo, J. Boronat, *Phys. Rev. B*, 86, 165409 (2012).
- [13] M. C. Gordillo, D. M. Ceperley, *Phys. Rev. B*, 58, 6447 (1998).