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Incidence of the Tomonaga-Luttinger liquid state on the NMR spin-lattice relaxation in carbon nanotubes

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Abstract – We report ^{13}C nuclear magnetic resonance measurements on ^{13}C-enriched single-wall carbon nanotube (SWCNT) bundles. The temperature dependence of the nuclear spin-lattice relaxation rate, $1/T_1$, exhibits a power law variation, as expected for a Tomonaga-Luttinger liquid (TLL). The observed exponent is smaller than that expected for the two-band TLL model. A departure from the power law is observed only at low T, where thermal and electronic Zeeman energy merge. Extrapolation to zero magnetic field indicates gapless spin excitations. The wide T range on which power law behaviour is observed suggests that SWCNT is so far the best realization of a one-dimensional quantum metal.

In a low-dimensional electronic system, restricted phase space and strong quantum fluctuations lead to emergence of unusual physical properties. A long studied example is the one-dimensional (1D) metal, where the conduction electrons are confined to move along the same direction. The standard Landau-Fermi liquid approach cannot be applied to such a system where the high probability of electron-electron scattering prohibits a description in terms of quasi-particles. The physical properties of a 1D metal in particular with a linear energy dispersion are rather described by the Tomonaga-Luttinger liquid (TLL) theory [1,2]. Characteristics of the TLL are the occurrence of power law divergences of the electronic response functions at low energies. These give rise to characteristic power law behaviour of experimental quantities as function of relevant energy scales such as frequency or temperature [3]. So far experimental studies have been limited by the difficulties in realizing the ideal 1D metallic state. Historically, the most studied candidates for such a realization were organic systems, *e.g.* conducting polymers like polyacethylene [4] and molecular conductors like TTF-TCNQ or Bechgaard salts $(TMTSF)_2X$ (ref. [5]). Despite their strong anisotropy, however, these materials still have a three-dimensional electronic structure. Therefore in practice the temperature range where the 1D behaviour can be observed is limited by dimensional crossover effects and resulting structural instabilities.

Carbon nanotubes (CNT) appear to be a natural candidates to realize 1D electronic systems, because of their enormous size aspect ratio. Experimentally, indeed, the TLL behaviour was observed in the electronic transport measurements on single-wall carbon nanotube (SWCNT) bundles [6]. One might notice, however, that the interpretation of conductivity measurements is not straightforward because of Coulomb blockade effects [7]. Subsequently, the photoemission spectroscopy on bundles of metallic nanotubes also revealed power law behaviour in the momentum distribution and the T-dependence of the density of states near the Fermi energy [8], both of which are characteristics of the TLL state.

NMR experiments also provide a sensitive probe of the low-temperature electronic state of 1D metals, because nuclear spin-lattice relaxation rate, $1/T_1$, directly measures the local spin excitations. In addition, this technique does not require any mechanical contacts to tubes, which can otherwise contaminate the electronic

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state. However, NMR experiment can be hardly performed on SWCNTs with small natural abundance of ^{13}C (1.1%). ^{13}C enrichment was done on double wall carbon nanotubes (DWCNT) using the "peapod" process of synthesis. Therein, ^{13}C NMR allows to probe the inner tubes, which are made out of ^{13}C-enriched C_{60} balls [9]. These measurements revealed that although one operates on a macroscopic sample involving DWCNTs with different geometries, quasi-uniform metallic properties were observed. Those were found to display 1D behaviour with eventually a TLL power law behaviour on a limited temperature range [10]. Remarkably, a clear uniform gap was detected below $T_g \simeq 20$ K, which should be associated with some instability of the 1D state.

In this letter, we report the results of ^{13}C NMR experiment on bundles of SWCNTs for which optimal processes were developed in order to produce ^{13}C-enriched samples with minimal impurity content [11]. The progress in isotope-engineering of SWCNTs allowed us to investigate a large temperature range without residual magnetic catalyst contamination. In contrast to the results on DWCNTs, we report here nearly gapless excitations even at low temperatures on SWCNTs. The comparison between the two systems strongly suggests that SWCNTs are a good 1D metal and opens many questions concerning the TLL state of such nanotubes.

The ^{13}C-enriched SWCNT samples used in this study were grown using the laser ablation growth method with an isotope-enriched graphite target (20–30% ^{13}C) and a mixture of non-magnetic Pt, Rh, and Re (ref. [11]). The as-prepared samples were purified by microwave heating, oxydation in air and washing in acids. A SWCNT content higher than 90% in weight was estimated by optical absorption. Raman spectroscopy indicated a mean tube diameter of 1.6 nm with a variance of 0.1 nm. The estimated length of the tubes appears to be 600 nm. Electron spin resonance spectroscopy indicated the absence of either magnetic catalyst particles or residual paramagnetic impurities. The fine powder samples were introduced into quartz glass tubes which were sealed under 20 mbar ^{4}He for the NMR measurements.

The nuclear spin-lattice relaxation rate $1/T_1$ was measured with the conventional saturation recovery method. The nuclear magnetization recovery curves do not fit the single exponential function anticipated when T_1 is uniform throughout the sample for a nuclear spin 1/2. To take the actual distribution of T_1 into account, we used a stretched exponential fit to the relaxation curves

$$\frac{M_0 - M(t)}{M_0} = A \exp\left(-(t/T_1)^{\beta}\right). \qquad (1)$$

Here $M(t)$ and M_0 are the nuclear spin magnetizations at delay t after saturation pulses and at equilibrium, respectively. A represents the initial saturation of the nuclear magnetization in the experimental conditions.

The temperature dependence of $(T_1T)^{-1}$ in SWCNTs in a magnetic field of 3.0 T is displayed in fig. 1 together with

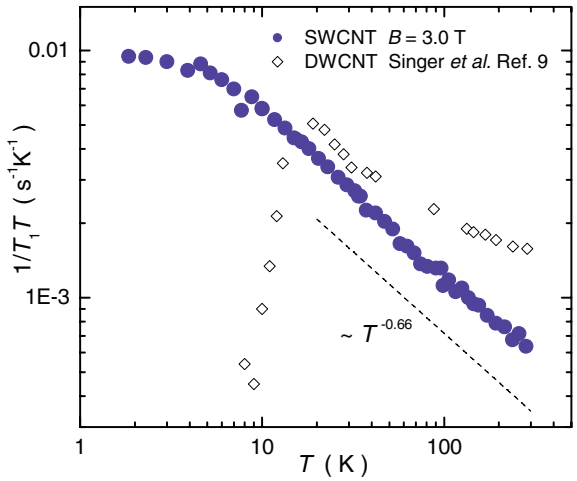

Fig. 1: (Colour on-line) T-dependence of $(T_1T)^{-1}$ in SWCNTs. For comparison similar data on DWCNTs is shown after ref. [9]. A gap is seen below 20 K for the latter and the data approaches a Fermi liquid variation at room T. In SWCNTs, the low-T gap is absent and the power law behaviour with $(T_1T)^{-1} \propto T^{-0.66\pm0.01}$ persists up to room T. The dashed line shows the latter behaviour.

that on DWCNTs after ref. [9]. A power law behaviour with $(T_1T)^{-1} \propto T^{-0.66\pm0.01}$ is observed in a large T range of 6–300 K, which is indicative of a TLL state maintained in a much larger T range than for DWCNTs.

The parameter β allows to describe the distribution of relaxation times in the sample. The fitted values of β were found T independent within experimental accuracy, as in the case of DWCNTs [9], with a similar average value of $\simeq$ 0.6 (fig. 2, inset). This rules out the possibility that the T_1 distribution arises from distinct parts of the sample with various electronic ground states, which would generate highly differing T-dependences of T_1. It is noteworthy that, for about 90% of the nuclear magnetization, the ratio between the longest and shortest T_1 at a fixed temperature is approximately 6, which is consistent with the previously reported value in both SWCNTs [12] or DWCNTs [9].

In order to prove that the exponent does not depend on the determination of T_1, we plot in fig. 2 the relaxation curves as a function of the product $t * T^{0.34}$. The relaxation curves obtained in the temperature range between 6 K and room temperatures fall onto a single curve, while that at 1.85 K shows a substantial deviation. The scaling by the factor $T^{0.34}$ confirms that all the distributed T_1's are proportional to $T^{0.34}$. This means that the T-dependence of the spin excitations is rather homogeneous in the sample and has a truly electronic origin, even if the actual values of T_1 are distributed. The relatively small distribution range as well as its independence on the type of tubes supports that the distribution originates in both SWCNTs and DWCNTs from the orientation of the nanotubes with respect to the applied field.

The electronic structure of SWCNTs displays two Dirac points, such as that of graphene. The corresponding linear

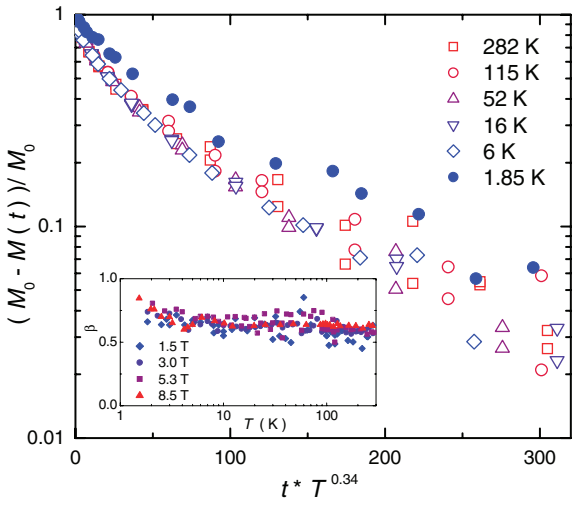

Fig. 2: (Colour on-line) Temperature-dependent magnetization recovery curves in the isotope-enriched SWCNTs *vs.* the product $t*T^{0.34}$ in 3.0 T magnetic field. Data at all temperatures except the lowest 1.85 K fall onto a single curve. This indicates that the distributed T_1's follows the same T-dependence. Inset: T variation of β values used for the magnetization recovery fits.

energy dispersion near Fermi energy should give rise to a two-band TLL behaviour, which differs markedly from the single-band TLL for metallic 1D chains. Correspondingly, the low-energy excitations of a two-band TLL is described by two spin and two charge modes with four Luttinger parameters: $K_{s\pm}$ and $K_{c\pm}$ [13]

Assuming that the applied field is small enough to maintain the spin rotational invariance, $K_{s\pm}=1$ and only the K_{c+} charge mode is affected strongly by the interactions [3,10], its value being different from 1. This allows to determine the exponents for the $(T_1T)^{-1}$ NMR relaxation rate. Generally, $1/T_1$ is expressed using the spin correlation function as

$$\frac{1}{T_1}=\frac{A_{\rm hf}^2}{2\hbar^2}\int {\rm d}\tau\cos\omega_0\tau\left\langle\frac{S_+(\tau)S_-(0)+S_-(\tau)S_+(0)}{2}\right\rangle, \tag{2}$$

where $A_{\rm hf}$ and ω_0 are the hyperfine coupling constant and the NMR frequency, respectively [14]. The calculations of the spin correlation function for this 1D state gives then the following T-dependence [3]:

$$\frac{1}{T_1T}\propto T^{\eta/2-2}, \qquad \text{with} \quad \eta=K_{c+}+3. \tag{3}$$

So the $-0.66(1)$ exponent found experimentally for $(T_1T)^{-1}$ would correspond to a non-realistic negative value $K_{c+}=-0.32(2)$. This points out that some of the assumptions made above are not valid. Within this two-bands approach realistic values of $K_{c+}=0.28$ or $K_{c+}=0.18$ were found, respectively, from conductivity and photoemission spectroscopy [6,8]. Let us point that, if the two charge modes were decoupled, the simple one-band TLL situation, where $\eta=2K_c+2$, would be valid and yield then $K_c=0.34(1)$ from our data. Notice that in this single-band case the K_c deduced from photoemission data would be 0.28, which indicates that the latter is less sensitive to the actual choice between one- and two-band models than our NMR data.

We note on the differences observed for the DWCNTs previously [9]. Therein, a similar power law T-dependence was observed only between 20 K and 50 K and the NMR relaxation rate appears to deviate towards a Fermi liquid-like behaviour around room T. We raise two possibilities to account for this. One is a subtle change in dimensionality due to the inter-wall coupling between the inner and outer nanotube shells, which could account for the suppression of the quantum fluctuations and stabilization of the Fermi liquid state. The other possibility is an increase in carrier density which would screen out the Coulomb interaction between the electrons and restore a Fermi gas picture, where the Luttinger parameter K_c is equal to 1. Although this might occur in electron doped nanotubes [15,16], it seems hard to obtain the required densities solely by thermal population of undoped CNT.

In addition to the different high-T behaviour in SW- and DWCNTs, there is a marked difference also at low T. For DWCNTs, a gap behaviour is observed below $T_g\simeq 20$ K, which is absent for the SWCNTs except for a small departure found below $T_X\simeq 6$ K.

The energy scale k_BT_g for such gap behaviours detected on spin excitations is found much smaller than that seen on charge excitations by scanning tunneling microscopy (STM) in SWCNTs [17]. As these charge gaps were found to decrease with increasing tube diameter, by analogy we tentatively assign the reduction of the gap size detected by NMR from the DWCNT to the SWCNT to a reduction of the nanotube curvature.

To better explore the possible existence of a small gap in SWCNTs we studied the field dependence of $1/T_1$ by taking data in four different fields from 1.5 T up to 8.5 T. The results are shown in fig. 3, where a similar high-T exponent is observed for all fields, although $1/T_1$ is found to increase slightly with decreasing field, as was the case as well in DWCNTs [9]. In contrast, while T_g was found therein to be field independent, here T_X (arrows in fig. 3) increases with the magnetic field, so that the power law variation persists down to the lowest temperatures in the lower fields. Since T_X extrapolates to zero at low field, as displayed in the inset of fig. 3, we conclude that the spin excitations are gapless in zero field. This also indicates that the T_1 behaviour found below T_X cannot be associated with a field independent energy scale, *e.g.* that associated with finite tube length effects. As T_X scales linearly with the applied field, we do find that $1/T_1$ scales (at least at low T) with the parameter $\Gamma=T/B$ as shown in fig. 4. The change of slope appears then for $\Gamma\simeq 1$ (K/T) that is for $\mu_BB\simeq k_BT$. Such a scaling is natural for independent free spins, however it is rather surprising here as we are considering an interacting electronic system for which the magnetic

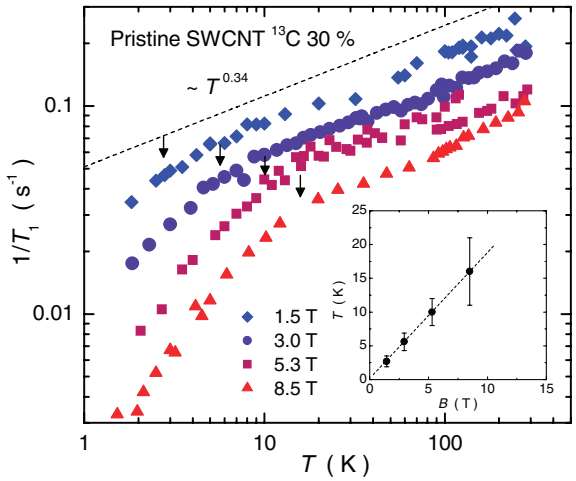

Fig. 3: (Colour on-line) T-dependence of $1/T_1$ in four different magnetic fields. The dotted line in the figure represents the curve for $1/T_1 \propto T^{0.34}$. The downward arrows indicate the temperatures, T_X, at which deviation occurs. The power law persists down to the lower T in the lower fields. Inset: field dependence of T_X. The dotted line is a guide to the eyes.

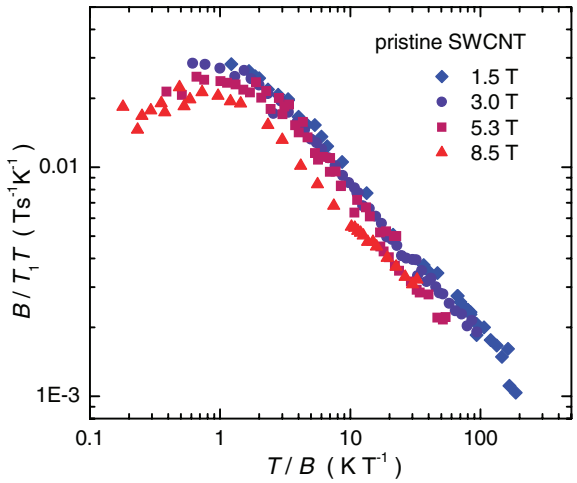

Fig. 4: (Colour on-line) $(T_1T)^{-1}$ plotted *vs.* the scaled temperature $\Gamma = T/B$. All the curves in four different fields fall onto a similar function. The broad peak is observed for $\Gamma \simeq 1$.

Zeeman term should only induce a change of behaviour for $\mu_B B$ comparable to the bandwidth.

When T_1 deviates from the high-T variation $1/T_1 \propto T^{0.34}$, the relaxation curve cannot be scaled by the same factor as seen in fig. 2, thus the low-T behaviour can indeed correspond to a distinct relaxation process. In the case of DWCNTs the change of β value below T_g was attributed to paramagnetic impurity relaxation in the gapped state. Indeed, presence of magnetic impurities in clean samples limits the measurable relaxation times T_1, yielding a minimum for $(T_1T)^{-1}$ at low T.

The observations done here in the absence of a gap are opposite, as $1/T_1$ is highly suppressed by application of a magnetic field at low T, an effect which cannot be assigned to out-of-chains impurities. One may still wonder whether the behaviour found could be governed by intrinsic impurities embedded in the SWCNTs. It is generally established that in correlated electron systems even non-magnetic defects, such as chain ends or substituted non-magnetic impurities reveal Curie moments which extend on the correlation length of the pure system [18]. In the present case, due to the slow decaying correlation functions, a moderate concentration of defects could nearly uniformly affect the TLL state. In that case the incidence of these moments would be totally suppressed in large fields, which would restore the behaviour which is intrinsic to pristine SWCNTs. It remains an open question whether the presence of defects could explain the deviation of the high-T exponent from the value expected for the two-band TLL state. It is also yet unclear whether the field dependence of $1/T_1$ seen at high T in fig. 4 could be attributed to a power law frequency dependence of the correlation function.

In conclusion, we performed ^{13}C NMR measurement on SWCNT bundles. We observed power law behaviour in the spin excitations in a wide temperature range, strongly indicative of a TLL state. A departure appears in the T-dependence of $1/T_1$ below a temperature T_X, which depend linearly on the external magnetic fields and extrapolate to $T = 0\,\mathrm{K}$, which evidences that the spin excitations are gapless down to very low T. These results indicate that SWCNTs are yet the best representation for 1D metallic behaviour. However, the observed exponents do not agree with theoretical expectations for the TLL state of undoped SWCNTs. While we are considering a series of experiments to complement the present results, we expect that they should stimulate theoretical efforts to account for the peculiar observations reported herein.

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