# Observation of phase transition from Tomonaga-Luttinger liquid states to superconductive phase in carbon nanotubes

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**We report the observation of change in one-dimensional Coulomb interaction between electrons in multi-walled carbon nanotubes (MWNTs). The results indicate occurrence of the phase transition from the Tomonaga-Luttinger liquid (TLL) states within repulsive Coulomb interaction to the superconductive (SC) phase within attractive Coulomb interaction mediated by phonon, as energy decreases. The small number of shells with current flow in the partially end-bonded MWNTs makes the observation possible.**

A carbon nanotube (CNT) is a one-dimensional (1D) molecular conductor within a ballistic charge -transport regime, in which no scattering factor for electrons exists. A variety of 1D quantum phenomena have been reported in CNTs. The Tomonaga-Luttinger liquid (TLL) state is a representative one [1–3], which is a collective phenomenon (e.g., showing spin-charge separation) that arises from the repulsive Coulomb interaction between electrons confined in a 1D ballistic conductance regime.

Many previous works have reported the TLL issues in CNT systems. It is known that the tunneling density of states $\nu(E)$ for the TLLs decreases following the power laws on energy decrease [i.e., $\nu(E) \propto E^{\alpha}$, where power $\alpha$ is the TLL exponent given by different formulae for different tunneling regimes: $\alpha^{bulk} = (g^{-1}+g-2)/8$ for tunneling to the bulk of CNTs from electrode and $\alpha^{end} = (g^{-1}-1)/4$ to the ends of the CNTs] [1, 2, 12]. The values of $g$, the Luttinger parameter, represent the types of electron-electron interaction [i.e., repulsive ($g < 1$) and attractive ($g > 1$) interactions and the non-interactive case ($g = 1$; Fermi liquid). Most previous works on CNTs have reported the strong repulsive Coulomb interaction (e.g., $g = \sim 0.2$).

In contrast, it is well known that the phonon-mediated attractive Coulomb interaction between electrons leads to Bardeen-Cooper-Schrieffer (*BCS*)-type superconductivity (SC) in 2D and 3D conductors. Therefore, how SC can occur and interplay with the TLL states in CNTs (1D conductors) has attracted considerable attention, because the repulsive Coulomb interaction of TLL states may destroy Cooper pairs at finite temperatures. The interplays have been reported from viewpoints of proximity-induced SC [7] and only theories in intrinsic SC [8–11, 14]. Here, we focus on the case of intrinsic SC.

Only a few groups have experimentally reported intrinsic SC in different types of CNTs [4 - 6] to date. Moreover, the possible interplay between the TLL states and intrinsic SC was only reported in our multi-walled CNTs (MWNTs) with the different number of layers for current flow [5]. The results were qualitatively consistent with the theory [8], which predicted that the TLL states could be suppressed by intertube electrostatic charge coupling of TLLs (i.e., sliding TLLs) in ropes of single-walled CNTs (SWNTs), resulting in the appearance of SC.

On the other hand, another theories predicted carrier-doping effect on transition to SC phase; 1.Carrier filling into the TLL states can drive the system to the SC phase via coupling with small-momentum acoustic phonon modes, because charge instabilities due to TLL states induced electron pairing [9] and 2.Doping effect into MWNTs led to a pairing instability for a large number of Fermi points and caused a transition from the TLL states to the SC phase [10]. These suggest that further experimental observation of the TLL is indispensable. In the present letter, we report the detailed observation of a transition

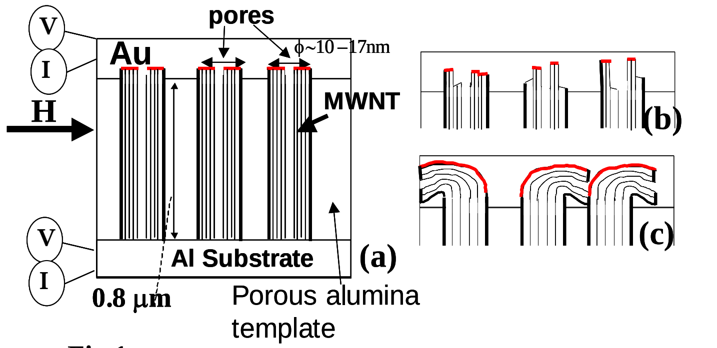


**Fig.1:** Schematic cross sections of array of MWNTs with **(a)** entirely end-bonded, **(b)** partially end-bonded, and **(c)** bulk junctions between Au electrode and top ends of MWNTs. The red lines indicate the interfaces between the MWNTs and the electrodes.

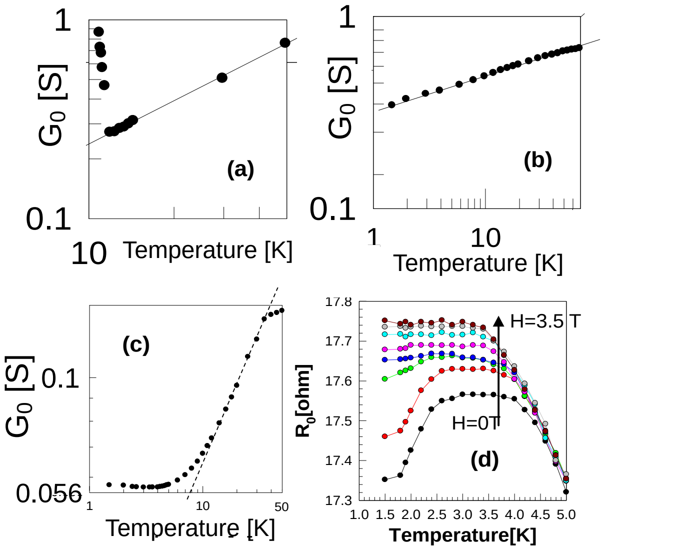


**Fig.2**: Doubly logarithmic scales of zero-bias conductance $G_0$ and temperature for **(a)** entire end, **(b)** bulk, and **(c)** partial end junctions. **(d)** Magnetic field dependence of zero-bias resistance $R_0$ as a function of the temperature, corresponding to (c).

from the TLL states to the SC phase in the partially end-bonded MWNTs. Mostly comparable strengths of the TLL states and SC phase, and charge instability in the MWNT allow us this observation.

Figure 1 shows the schematic cross sections of the array of MWNTs with (a) an entirely end-bonded junction ($N$ = 9; where $N$ is the number of layers with current flow), (b) a partially end-bonded junction ($1 < N < 9$), and (c) bulk junction ($N$ = 1) between the Au electrode and the top ends of the MWNTs [5]. High-quality MWNTs were synthesized by chemical vapor deposition using an Fe/Co catalyst and methanol gas in the nanopores of the alumina template, and each junction was formed by cutting the top portion of the MWNTs in different ways [5].

Figure 2 shows the doubly logarithmic scales of zero-bias conductance $G_0$ and temperature for the three different junctions shown in Fig.1. The observed power law behaviors with power $\alpha$ in any junctions ($G_0 \propto T^{\alpha}$; $\alpha$ = 0.7, 0.3, and0.8 in (a), (b), and (c) respectively) are in excellent agreement with the previous reports of TLL states in CNTs [2, 5]. Here, we reported the finding of SC with $T_c$ as high as 12 K by making current flow through all the layers of a MWNT in the entirely end-bonded MWNTs (Fig.1(a)) [5]. Because TLL states of the MWNT were strongly suppressed due to the interlayer electrostatic coupling for a large value of $N$ = 9 in the MWNTs, SC phase could suddenly overcome the TLL at $T_c$ = 12 K [8]. This corresponds to Fig.2(a), in which TLL phase existing at $T > T_c$ abruptly transits to SC phase at $T_c$. In the bulk-junction (Fig.1(c)), TLL phase existed in the entire temperature range as shown in Fig.2 (b) and SC could not appear, because of the value of $N$ = 1.

In contrast, in partially end-bonded MWNTs (Fig.1(b)), a sign of SC (i.e., slight and gradual resistance drop; Fig.2(d)) was detected only at low temperatures, because the strengths of the TLLs and SC were comparable due to the small $N$ value. With an increase in the magnetic field, the drop in resistance $R_0$ disappears rapidly. This behavior agrees with that of conventional superconductors.

Figure 2(c) corresponds to this result. The power law is observable up to T = 40 K for $\alpha$ = ~0.7, while it gradually starts to deviate below T = ~12 K. At T < ~5 K, it saturates completely. Subsequently, a small increase in $G_0$ due to SC occurs at T = ~2.5 K. This indicates a possibility of an occurrence of phase transition from the TLL phase to the SC phase with decreasing temperature, because the saturation of power laws implies a gradual decrease in $\alpha$ value and therefore an increase in the $g$ value from $g$ = ~0.25 (<1 for repulsive Coulomb interaction) towards $g > 1$ (for attractive one) with decreasing temperature, following the formula of TLL state for the end contact $\alpha^{end} = (g^{-1}-1)/4$. Thus, it can be interpreted that the SC phase appears at T < ~2.5 K as a result of the increased $g$ value.

Here, we show more precise observation result of this transition with respect to voltage and energy dependence in Fig.3. Figure 3(a) shows the doubly logarithmic scales of differential conductance and voltage as a function of the temperature, which corresponds to Fig.2(c). The TTL states can be discussed for a high-voltage region, that is, for $eV >> kT$. Certainly, a sign of power laws can be observed

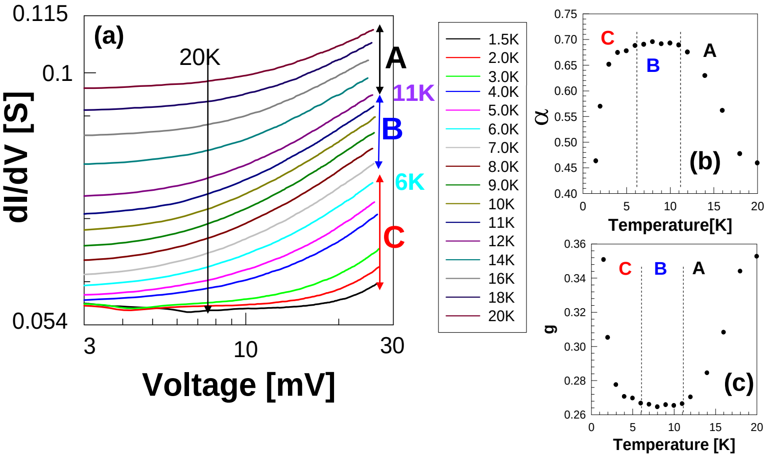


**Fig.3: (a)** Doubly logarithmic scales of differential conductance and voltage as a function of the temperature, which corresponds to Fig.2(c). **(b)** The values of α as a function of temperature estimated from V > ~10 mV in Fig.3(a). **(c)** The value of Luttinger parameter $g$, which was estimated from the α values in Fig.3(b) by using the formula of TLL state with end junctions $\alpha^{end} = (g^{-1}-1)/4$, as a function of the temperature.

above $V$ = ~10 mV at each value of temperature, although the range of data may be too small to definitely conclude the presence of power laws. It should be noted that the power law behaviors strongly depend on the temperature values.

Figure 3(b) shows the values of α as a function of the temperature estimated from Fig.3(a). They can be evidently classified to the following three regions, as temperature decreases; (A) T > 12 K for increasing α values, (B) 12 K ≥ T > 6 K for constant α values of ~0.7, and (C) T ≤ 6 K for a drastic decrease in α values. A conductance peak around $V$ = 0 due to the appearance of the SC phase can actually be observed at T ≤ 3 K in the low-temperature region (C), as reported in [5]. Importantly, these behaviors and critical temperatures are in excellent agreement with those in Fig.2 (c). In particular, the region (C) stresses that the SC phase appears as a result of an increase in the $g$ value as well as the saturation of power laws at T < 12 K in Fig.2(c).

In order to reconfirm this, Fig. 3(c) shows the value of $g$, which was estimated from the α values in Fig.3(b) by using the formula of the TLL state with end junctions. We can certainly reconfirm that the $g$ value is constant at ~0.26 in region (B), whereas it abruptly increases towards 1 in region (C). This can serve as direct evidence for the transition from the TLL phase to the SC phase.

Experimental observation of TLL states and its confirmation by theory need ν(E) in CNTs as mentioned in introduction, while SC transition and Cooper pairs may not favor such a tunnel junction. Kane's theory [12], however, predicted that even attractive Coulomb interactions could lead to power law behaviors similar to those observed in the TLL states [1,2] along with perfect transmission via tunnel junction. Thus, the present result is consistent with this theory.

In contrast, whether such power laws can act as actual evidence for the TLL states has been discussed, particularly by comparing with the Coulomb blockade coupled with its external electromagnetic environment and 1D localization [2, 3]. Thus, a more careful analysis becomes necessary. Here, in Fig.4(a), we replot the data set of Fig.3(a) on doubly logarithmic scales for differential conductance normalized by $G_0$ vs. normalized voltage energy $eV/kT$, which is one of the typical formulas for the TLL states [13]. The used data set is the same as that in Fig.3. Surprisingly, in this case, the entire data collapse suitably onto a single universal curve at T ≥ ~7 K in contradiction to Fig.3(a). This agrees with just the feature reported in previous works for TLL states [1, 2, 13]. As shown by the red dotted line, this universal curve can be fit by the following relationship for TLL states [13],

$$\frac{G(V,T)}{G(V=0,T)} = \cosh(\gamma\frac{eV}{2kT})\frac{1}{\left|\Gamma(\frac{1+\alpha}{2})\right|^2}\times\left|\Gamma(\frac{1+\alpha}{2}+\gamma\frac{ieV}{2\pi kT})\right|^2 \qquad (1)$$

where $V$ is the applied voltage; Γ(x), the Gamma function; $k$, the Boltzmann constant; and γ, the inverse number of the measured junctions $M$ weighted by their resistance [13]. For $M$ junctions in series, the value of γ should be within $\gamma = 1/M$. The best fit gives the parameter γ = ~0.7, which is mostly in good agreement with $\gamma = 1/M = 0.5$ for $M = 2$ of our individual MWNTs with two end junctions. Therefore, we conclude that the universal curve can be actually attributed to the TLL states.

The inset of Fig. 4(a) shows the values of α as a function of the temperature estimated from the main panel of Fig.4(a). It is important to note that the α value is constant at ~0.67 for every temperature range

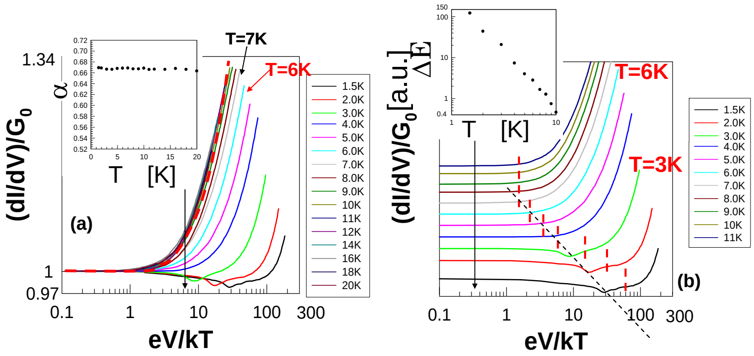


**Fig.4:** **(a)** Data set of Fig.3(a) replotted to doubly logarithmic scales on differential conductance normalized by $G_0$ vs *eV/kT*, corresponding to formulas for TLL states [13]. The red dotted line gives the best fitting result by eq.(1). **Inset**: power value α vs. temperature estimated from main panel. **(b)** Shifted values of $(dI/dV)/G_0$ of Fig.4(a) to arbitrary unit on Y-axis. The dotted line connects the edges of the conductance peaks caused by SC. **Inset**: $\Delta E_c = E_c\,(T) - E_c\,(T = 7\text{ K})$, where $E_c$ is the critical boundary between the saturation and power law regions, as shown by the red dotted lines in the main panel, as a function of the temperature on doubly logarithmic scales..

(even at T ≤ ~6 K). This result stresses that repulsive interaction still remains even at T ≤ 6K in contradiction to Fig.3(b) and (c). On the contrary, we importantly find a deviation from the universal curve at T ≤ 6 K in Fig.4(b), which has the Y-axis value shifted by each *T*. This deviation originates from a monotonic increase in the low voltage-energy saturation region (ie., at *eV/kT* < 6 at T = 7 K) in the universal curve at T ≤ ~6K, as shown in Fig.4(b).

The inset of Fig.4 (b) shows $\Delta E_c$ [$= E_c\,(T) - E_c\,(T = 7$ K)], the low voltage-energy saturation region, as a function of temperature on doubly logarithmic scales. $\Delta E_c$ actually increases with a decrease in temperature, following the power laws. It should be noted that the value of the critical temperature of 6K is in excellent agreement with that for region (C), where the α value starts to decrease in Fig.3(b) (i.e., the *g* value starts to increase in Fig.3(c)) and the saturation region in Fig.2(c).These agreement strongly suggest that the deviation at T ≤ ~6 K in Fig.4(b) is strongly associated with the appearance of phonon-mediated attractive Coulomb interaction due to the SC phase.

Figure 4(b) reveals that the increase in the saturation region is evidently caused by appearance of the conductance peak (shown by the dotted line) due to the SC phase, in particular at T ≤ 3 K. Moreover, the critical temperature of 6 K for the appearance of deviation in Fig.4(b) is in excellent agreement with those for region (C) in Fig.3(c) and for Fig.2(c), as mentioned above. From this viewpoint, the SC phase potentially exists even at 3 K < T ≤ 6 K, although the conductance peak cannot be observed due to obstruction of the TLL states. These results strongly suggest that the emergence of the SC phase leads to a deviation from the TLL states.

In the conventional theory for TLL states, the low voltage-energy saturation region means the regime for $eV/kT < \Delta E = hv_F/L$, where $v_F$ and $L$ are the Fermi velocity and tube length of 1D conductors, respectively [17]. ΔE is the energy spacing of the quantized electronic orbital formed in the CNTs within a ballistic charge transport regime. Here, $v_F$ is given by $hk_F/m^*$, where $k_F$ and $m^*$ are the Fermi wave length and effective mass in the CNTs, respectively. However, these values for $\Delta E = hv_F/L$ should be basically independent of the change in temperature. Indeed, the previous studies on TLL states in CNTs reported that the saturation regimes fall onto an universal curve (i.e., as shown at T ≥ 7 K in Fig.4(a)) in all temperature ranges.

From this viewpoint, the appearance of a conductance peak due to the SC phase can be interpreted as the appearance of a superconducting gap Δ in addition to ΔE, because the saturation regime means ΔE. Since the present measurement uses two terminal methods, Δ cannot be detected conventionally. However, the format for Fig.4 and analysis make this detection possible. Here, a value of *eV/kT* = ~100 at T = 0.1K can be obtained from values of *eV/kT* at where the conductance peak due to SC disappears (i.e., from the dotted line in Fig.4(b)). Hence, *eV* = ~1 mV at T = 0.1 K can be estimated. Importantly, this value is in good agreement with $\Delta = 1.76\ kT_c$ of *BCS* theory, when $\Delta = eV = $ ~1 mV is assumed for $T_c = 12$ K [5]. This result strongly suggests that the emergence of Δ yields a deviation from the TLL states.

In spite of the emergence of this Δ, however, α = ~0.67 is maintained constant, and the repulsive Coulomb interactions still survive even at T ≤ 3K at high voltage energies, as mentioned above. Since eq.(1) for the TLL states and Fig.4 give a configuration that is more accurate than that of Fig.3, in which the normalization by *kT* was not considered, this result is more precise than finding of the drastic increase in the value of *g* toward *g* = 1 in Fig.3. Because $G_0$ of Fig.2(c) is around zero voltage, the critical temperature of 6 K for the saturation region is consistent with that in Fig.4.

This result of Fig.4 implies a possibility that the charge instabilities due to the TLL states at high energies induce electron pairing, leading to Δ at low voltage energies ($< \Delta E = hv_F/L$). Indeed, low energy theories predicted a transition from the TLL states to the SC phase in (ropes) of SWNTs under suppressed TLLs [11,14]. In particular, ref. [9] predicted that increasing the filling factor *n* towards half filling in the TLL states could lead to the SC phase via coupling with small-momentum acoustic phonon modes near the Wentzel-Bardeen singularity in the 1D system and also the correlation of the phase transition with *n* and effective electron-phonon coupling parameter $\sim(1/c)(g/u_\rho)^{1/2}$ where $u_\rho$ is the charge velocity.

Our samples have a possibility of occasional boron doping, which is used for the activation of the chemical reaction of the Fe/Co catalyst [5] as well as for the case of [15, 16]. If this doping condition could be near half filling under arbitrary on-site repulsion *U* reduced by interlayer electrostatic charge coupling, an increase in the value of $(1/c)(g/cu_\rho)^{1/2}$ toward 1 can result in efficient phase transition from TLLs to the SC phase according to [9]. Since a decrease in the voltage energy can lead to a decrease in the $u_\rho$ value, this transition can actually occur in spite of the constant *g* value (<1) at high voltage energies. Moreover, the doping effect in MWNTs can cause a transition from TLLs to the SC phase due to many Fermi points [10]. Although further quantitative investigation is expected, the present phenomena shed light on understanding of 1D electron correlations.

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