Supplementary Materials

for

Observation of high T_c one dimensional superconductivity in 4 Angstrom carbon nanotube arrays

Bing Zhang, Yang Liu, Qihong Chen, Zhiping Lai, Ping Sheng

One dimensional fluctuation superconductivity

Introduction and relevance to the experimental data

The definition of a one dimensional (1D) superconductor is that the superconducting coherence length is larger than the cross sectional dimension of the 1D wire. When that happens, the superconducting wavefunction can be regarded as a constant at any given cross section, but can vary along the length direction x of the wire. Moreover, since any variation in the magnitude of the superconducting wavefunction, which represents the superconducting condensate density, requires a much larger energy than the phase of the wavefunction, hence it is usually the case that in the theory of 1D superconductors only the phase variation is considered as a function of x. In a long 1D superconductor (long meaning compared to the coherence length), the end effect of the wire can be neglected, hence its physics may be described by a ring, in which periodic boundary condition on the phase can be imposed. When that happens, only a phase change of 2π is possible. But such a phase change would require the magnitude of the wavefunction vanish at least at one point along the length direction, which requires energy. Hence there is an energy barrier between 2π phase change which is proportional to the cross sectional area of the wire. When the cross section is thin, the energy barrier is low, and thermal fluctuations can cause the phase changes in a regular manner, statistically speaking. Such fluctuation-initiated phase changes are called the “phase slip” mechanism. When that happens, the Josephson relation (see below) dictates a voltage would appear, which is equivalent to say that resistance appears. The above is a qualitative description of the phase slip mechanism and its relation to the appearance of resistance in 1D superconductors. Below we give a more detailed mathematical description of the theory behind it, and the behavior of the predicted resistance that appears as a result of the phase slip mechanism. In short, what the theory predicts are (1) the resistance should vary smoothly as a function of temperature, and (2) there should be a nonlinear current-voltage (I-V) behavior at small bias currents. Both of these predicted behaviors are seen in our experiments, consistent with the theory of 1D superconductors.

The Ginzburg-Landau equation

The properties of the 1D superconductors can be described by the Langer–Ambegaokar–McCumber–Halperin (LAMH) theory[1,2], which is based on the Ginzburg-Landau (GL) equation. For the 1D superconductivity, dissipation occurs when thermal fluctuation causes the order parameter wavefunction to vanish at some point along the wire, and the phase of the wavefunction to change by 2π. As a consequence, the 1D superconductor can have finite resistance at finite temperature below the transition temperature. In general, the diameter of the 1D superconductor is much smaller than the coherence length. Thus the parameters of GL can be regarded as a constant over the cross-sectional area and are a function of x only, where x denotes the axial coordinate. The Ginzburg-Landau free-energy functional has the form[3]:

$$F[\psi(x)] = \sigma \int dx \left[\frac{\hbar^2}{2m^*} \left| \nabla \psi(x) \right|^2 + \alpha \left| \psi(x) \right|^2 + \frac{\beta}{2} \left| \psi(x) \right|^4 \right], \qquad \text{(S1)}$$

where σ is the cross-sectional area of the 1D superconductor, α and β are the phenomenological parameters. The time evolution of ψ is governed by the time-dependent Ginzburg-Landau equation:

$$\gamma \frac{\partial}{\partial t} \psi = -\frac{1}{\sigma} \frac{\delta F[\psi]}{\delta \psi} + \zeta = \frac{\hbar^2}{m^*} \nabla^2 \psi - 2\alpha\psi - 2\beta \left| \psi \right|^2 \psi + \zeta, \qquad \text{(S2)}$$

where γ is a viscosity coefficient and ζ is the Langevin white noise, intended to model thermal fluctuations. The noise leads to a random variation of ψ. It is convenient to use the dimensionless form in computation:

$$F[\bar{\psi}(\bar{x})] = \int d\bar{x} \left[\frac{1}{2} \left| \bar{\nabla} \bar{\psi}(\bar{x}) \right|^2 - \frac{1}{2} \left| \bar{\psi}(\bar{x}) \right|^2 + \frac{1}{4} \left| \bar{\psi}(\bar{x}) \right|^4 \right]. \tag{S3}$$

The over-bar denotes the dimensionless qualities, obtained with F scaled by $\sigma\xi\alpha_0^2(T_c - T) / \beta = \varepsilon_0$, which is the superconducting condensation energy for a volume $\sigma\xi$, ψ is scaled by $\sqrt{-\alpha / \beta}$ and x is scaled by the correlation length $\xi(T)$. The dimensionless form of the GL equation is obtained from Eq. (S3) through functional variation:

$$\frac{\partial}{\partial \bar{t}} \bar{\psi} = -\frac{\delta \bar{F}[\bar{\psi}]}{\delta \bar{\psi}} + \bar{\zeta} = \bar{\nabla}^2 \bar{\psi} + \bar{\psi} - \left| \bar{\psi} \right|^2 \bar{\psi} + \bar{\zeta}, \tag{S4}$$

where time is scaled by $\tau(T) = -\gamma / \alpha$.

Solution for the metastable superconducting current states

For a closed superconducting ring we can use the periodic boundary condition $\psi(-l/2) = \psi(l/2)$, where l is the circumference of a ring. Then we can get the metastable current carrying states ψ_n from the stationary Ginzburg–Landau equation

$$0 = \frac{\partial}{\partial \bar{t}} \bar{\psi} = \bar{\nabla}^2 \bar{\psi} + \bar{\psi} - \beta \left| \bar{\psi} \right|^2 \bar{\psi}, \tag{S5a}$$

which yields the solution

$$\bar{\psi}_n = \sqrt{1 - k_n^2} e^{ik_n x}, k_n = 2\pi n / l, \tag{S5b}$$

where k_n is the wave vector and n is an integer, called the winding number.

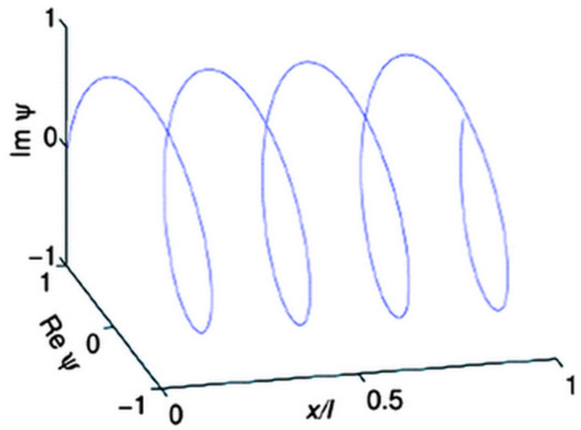

Figure S1. The order parameter ψ for a 1D superconductor with a winding number of four[4]. Since the magnitude of the wavefunction is regarded as rigid, a helical configuration naturally emerges to depict the phase change along x.

Owing to the fact that the variation of wave function magnitude involves much larger energy than the phase variation, the magnitude of wave function is rather rigid at a fixed temperature below T_c. In order to depict such a state a picture of this meta-state is shown in figure S1, which involves only the phase variation as a function of x. In quantum mechanics, the current density in the $\bar{\psi}_n$ state is given by the spatial derivative of the wavefunction:

$$J_n = \bar{\psi}^* \frac{\partial}{\partial x} \bar{\psi} = (1 - k_n{}^2) k_n, \qquad \text{(S6)}$$

where $|k_n| < k_c$, with $k_c = 1/\sqrt{3}$ being the critical upper bound for k_n. Larger winding number n corresponds to larger carrying current as well as a higher free energy of the metastable state. As illustrated in figure S2, the scaled free energy F is plotted as a function of the arc length s in the $\psi(x)$ functional space. It is evaluated along the minimal energy path connecting a sequence of the meta-stable (−8, −7, …, −1, 1, …, 7, 8) and stable states (n = 0). This figure was numerically evaluated by using the string method[4].

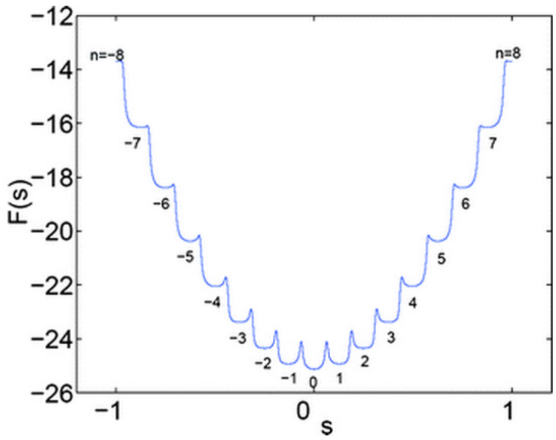

Figure S2. Free energy F evaluated along the minimal energy path connecting a sequence of the meta-stable (−8, −7, …, −1, 1, …, 7, 8) and the stable state (n = 0). Here s represents the arc length along the minimal energy path in the functional space of $\psi(x)$. Each metastable minimum represents a winding number configuration[4]. It should be noted that the barrier height separating the different metastable states, each characterized by n, decreases with increasing current level (increasing n).

We can see that there is a potential barrier between neighboring metastable states. Moreover, this potential barrier becomes larger for the lower current-carrying states. This will have implications for the nonlinear I-V characteristic as a function of the bias current, described below. The carrying current does not generate any voltage if the wave function remains in a metastable state, which means that the system is still superconducting. Nevertheless, in the presence of thermal fluctuations, one metastable state can cross the potential barrier and transit to another metastable state (more probably the lower free energy one). Therefore, these metastable states just have a finite lifetime in a thermal bath. Let us consider a 1D superconductor which is connected to a constant (bias) current source. If a metastable state n transits to the lower free energy metastable state $n-1$, then the carrying current of the 1D superconductor will decrease. However, the constant (bias) current source will push the system back to the metastable state n again in order to maintain the current at a fixed value. Hence dissipation would occur in this process, which is equal to the work done by the external (constant current) source. Another way to explain the same thing is that the thermally induced transitions between the metastable states will generate a voltage. The magnitude of the voltage is described by the following Josephson relation:

$$2\pi\Gamma_{ps} = 2eV/\hbar, \tag{S7a}$$

with

$$\Gamma_{ps} = \Omega \exp(-\Delta F / k_B T), \tag{S7b}$$

where Γ_{ps} is the phase slip rate, Ω is the transition rate pre-factor, and ΔF is the energy barrier. There is a temperature dependence of the energy barrier, given by

$$\Delta F = \left(8\sqrt{2}/3\right)\left(H_C^2/8\pi\right)\sigma\xi,$$

where H_C and ξ are the thermodynamic critical field and the coherence length, $H_C = H_{C0}\left[1-(T/T_C)^2\right]$ and $\xi = \xi_0/\left(1-T/T_C\right)^{1/2}$. we can see that the energy barrier is proportional to the cross section area σ of the superconductor. After simplification we get

$$\frac{\Delta F}{k_B T} = \frac{\sqrt{2}H_{C0}^2\sigma\xi_0}{3\pi k_B T_C}\frac{T_C}{T}\frac{\left[1-\left(T/T_C\right)^2\right]^2}{\left(1-T/T_C\right)^{1/2}} = A\frac{T_C}{T}\left(1+\frac{T}{T_C}\right)^2\left(1-\frac{T}{T_C}\right)^{3/2}, \tag{S8}$$

where $A = \frac{\sqrt{2}H_{C0}^2\sigma\xi_0}{3\pi k_B T_C}$ is a dimensionless constant. By definition the resistance is the ratio of voltage divided by the bias current that is supplied by the current source. Hence

$$R = V/I = \hbar\pi\Gamma_{ps}/eI = R_N \exp\left(-\Delta F/k_B T\right) = R_N \exp\left[-A\frac{T_C}{T}\left(1+\frac{T}{T_C}\right)^2\left(1-\frac{T}{T_C}\right)^{3/2}\right],$$

or

$$R = R_N \exp\left[-A\frac{T_C}{T}\left(1+\frac{T}{T_C}\right)^2\left(1-\frac{T}{T_C}\right)^{3/2}\right]. \tag{S9}$$

where R_N denotes the normal state resistance. With decreasing temperature the resistance decreases smoothly if the parameter A is small, i.e., small cross sectional area. For a fixed temperature, the resistance would be larger for higher bias current-carrying states as a consequence of the increased transition rate.

Smooth temperature variation of resistance and the dV/dI dip

The basic concept of LAMH theory gives us a simple picture about how a 1D superconductor acquires finite resistance. From Eq. (S9), it is easily seen that the resistance must decrease as temperature decreases, in a continuous and smooth manner. Moreover, since the barrier ΔF is large for small bias current and smaller for large bias current as noted above, it follows that the I-V characteristic should be nonlinear (since ΔF appears in the exponent), i.e., the resistance should be small at small bias current and increases with increasing bias current. That is precisely the differential resistance dip observed in our experiment.

It is noteworthy that the height of the potential barriers separating the meta-stable states is directly proportional to the cross-sectional area of 1D superconductor. Therefore, the transition rate exponentially decreases with an increasing cross-sectional area and the resistance vanishes as the system approaches 3D.

References

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