Bulk and Boundary Zero-Bias Anomaly in Multiwall Carbon Nanotubes

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We compute the tunneling density of states of doped multiwall nanotubes including disorder and electron-electron interactions. A nonconventional Coulomb blockade reflecting nonperturbative Altshuler-Aronov-Lee power-law zero-bias anomalies is found, in accordance with recent experimental results. The presence of a boundary implies a universal doubling of the boundary exponent in the diffusive limit.

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Carbon nanotubes provide a remarkable and exciting arena for mesoscopic transport phenomena involving strong electron correlations [1]. Recent experiments on single-wall nanotubes (SWNTs) have established the ballistic nature of SWNT transport and revealed the Luttinger liquid (LL) behavior of one–dimensional (1D) interacting fermions [2]. However, the situation is less clear for multiwall nanotubes (MWNTs), which are composed of several (about ten) concentrically arranged graphite shells, where experiments seem more consistent with diffusive transport [3], e.g., showing typical weak localization features in the magnetoconductance.

Quite remarkably, several experimental observations of MWNTs do not seem to fit into the framework of existing theories. The most prominent example concerns the pronounced power-law zero-bias anomaly of the tunneling density of states (TDOS) found at low-energy scales, $E \lesssim 0.1$ eV [4,5],

$$\nu(E) \sim E^{\alpha}, \qquad \alpha \approx 0.3\,. \tag{1}$$

Furthermore, the TDOS at the end of the MWNT, while still of power-law form, is characterized by the boundary exponent $\alpha_{\rm end} \approx 0.6$. In this Letter, we show that these results can be understood in terms of a particularly effective and nonconventional *Coulomb blockade* (CB) for tunneling into a strongly interacting disordered metal. Charge propagation on the MWNT is then effectively two dimensional (2D), but for very low energy scales not probed in Ref. [5], $E < E^*$ with E^* in Eq. (13) below, a crossover to 1D pseudogap behavior [6] is expected.

The key ingredient in CB theory is the probability $P(E)$ that a tunneling electron excites electromagnetic modes with energy E in the system [7]. The theory is meaningful if these modes are harmonic, and then $P(E)$ directly determines the TDOS [7],

$$\frac{\nu(E)}{\nu_0} = \int_{-\infty}^{\infty} dE' \, \frac{1 + \exp(-E/k_BT)}{1 + \exp(-E'/k_BT)} \, P(E - E')\,, \tag{2}$$

where ν_0 is the noninteracting DOS. The probability $P(E)$ is the Fourier transform of $\exp[J(t)]$, with the phase correlation function ($\hbar = 1$),

$$J(t) = \int_0^{\infty} d\omega \, \frac{I(\omega)}{\omega} \{\coth(\omega/2k_BT)[\cos(\omega t) - 1] - i \sin(\omega t)\} \tag{3}$$

for a spectral density $I(\omega)$ of electromagnetic modes. For simplicity, we now focus on the zero-temperature case. Provided $I(\omega)$ remains finite for low frequencies, Eqs. (2) and (3) then straightforwardly lead to the power law (1) with exponent $\alpha = I(\omega \to 0)$.

In a conventional CB system, $I(\omega)$ is phenomenologically parametrized in terms of the total impedance $Z(\omega)$ [7], and one obtains $\alpha = Z(0)/(h/2e^2)$. Such a transmission line model directly explains the doubling of the end exponent, since in the bulk case, one has effectively two resistances in parallel as compared to the end case. Applying this model to MWNTs, however, one finds rather small values for α, and, in addition, the observed voltage dependence cannot be reproduced [5]. On the other hand, for a LL, the elementary excitations are harmonic, $I(\omega)$ is known, and hence $P(E)$ can also be computed exactly. The resulting exponents can be written in terms of the standard interaction parameter g, and the ratio $\alpha_{\rm end}^{\rm LL}/\alpha^{\rm LL}$ is g dependent and always larger than 2 [8,9]. In MWNTs, g is modified by inner-shell screening, and the relation between $\alpha^{\rm LL}$ and g is affected by the available subbands [10]. Estimating $\alpha^{\rm LL}$ and $\alpha_{\rm end}^{\rm LL}$ for the situation in Ref. [5], they are at least 1 order of magnitude smaller than observed. Hence neither conventional CB nor LL theory can explain these data.

For a ballistic system, the full crossover in the CB between a (single-channel) LL and a (many-channel) classical resistor was worked out in Ref. [11]. The results of this paper imply that it is crucial to take disorder into account here. We thus have to (i) establish the harmonic nature of the electromagnetic modes, (ii) compute the low-frequency spectrum $I(\omega)$ and hence the exponent α, and (iii) compute the end exponent. Note that a perturbative treatment of the interactions is not sufficient, as the power law (1) is inconsistent with conventional (1D or 2D) Altshuler-Aronov-Lee (AAL) predictions for the TDOS [12].

However, 2D AAL logarithmic dependencies have been observed for MWNT bundles, which presumably are characterized by weaker interactions [13].

The main difference between MWNTs and SWNTs, apart from the larger radii of MWNTs, $R \approx 4-10$ nm, stems from the presence of inner shells. Although intershell tunneling is largely suppressed for a number of reasons [14], and hence transport proceeds only through the outermost contacted shell [3], inner shells cause a screening of the electron-electron interaction. For a computation of the TDOS, the latter effect, as well as spin and Fermi (K) point degeneracy [1], can be included by a renormalization of the electron-electron interaction potential $U(\vec{q})$ [10], and hence we consider spinless electrons with only one K point in what follows. Since different shells always have incommensurate lattices, a *quasiperiodic* ionic potential from inner shells acts on outermost-shell electrons. The effect of such a potential is very similar to a random potential described by a mean-free path $\ell = v\tau$ [15], which can be estimated from a disordered tight-binding approach using random on-site energies with variance σ_E^2. For nearest-neighbor hopping t_0 and $2N + 1$ subbands (see below), one finds [10]

$$\ell = (t_0/\sigma_E)^2 R/(2N + 1) \approx 10R\,. \tag{4}$$

Here $\sigma_E \approx t_0/10$ corresponds to the hopping strength between adjacent shells, and $N \approx 5$. Therefore disorder is present even in impurity-free MWNTs. In addition, "true" disorder imposed by imperfections, substrate inhomogeneities, or defects can be important. Using Matthiessen's rule, $\ell^{-1} \to \ell^{-1} + \ell_0^{-1}$, where ℓ_0 is the mean-free path due to "true" disorder. Typical values of $\ell \approx 5-100$ nm were reported in Refs. [3–5]. Hence disorder is still "weak," $k_F\ell \gg 1$, and the possibility of a diffusive phase of interacting electrons must be discussed. Doped MWNTs are in between the 1D and 2D limits and may be expected to show diffusive behavior over a wide energy range, where the Anderson localization expected for truly 1D disordered systems has not yet set in. We mention in passing that the phase relaxation length is $\ell_\phi \approx 500$ nm at 2 K, with the usual T dependence due to electron-electron interactions [4].

The band structure of a clean nanotube is described by a Dirac "light cone," $E(\vec{k}) = v|\vec{k}|$, with $\vec{k} = (k, k_\perp)$ and quantized transverse momentum, $k_\perp = n/R$, where $n = -N, \ldots, N$ and $N = [k_F R]$. The Fermi velocity is $v = 8 \times 10^5$ m/s, and the number $2N + 1$ of 1D subbands arising from periodic boundary conditions around the circumference is determined by the doping level μ via $k_F = \mu/v$. Since MWNTs studied experimentally so far are characterized by rather large doping, $\mu \approx 0.5$ eV [16], a typical value is $N \approx 5$. The nth subband is characterized by Fermi velocity and momentum,

$$v_n = v\sqrt{1 - (n/k_F R)^2}, \qquad k_n = k_F v_n/v\,. \tag{5}$$

The theoretical description for small μ is quite intricate and will be given elsewhere, as the disorder causes logarithmic divergences of the self-energy due to the vanishing DOS of the Dirac cone [17]. Fortunately, these complications are absent for the case studied below, $k_F R \gg 1$. In the following, we focus on energy scales $E < v/R$, where it is sufficient to take a fixed N and thereby ignore van Hove singularities associated with the opening of new 1D bands as the energy varies.

Let us start with the bulk TDOS, where standard diagrammatic perturbation theory [12] adopted to the MWNT geometry is quite illuminating. The disorder-averaged Greens function is

$$G_{R/A}(E, \vec{k}) = [E + \mu - E(\vec{k}) + i\,\mathrm{sgn}(E)/2\tau]^{-1}, \tag{6}$$

and hence the noninteracting DOS is

$$\nu_0 = -\frac{\mathrm{Im}}{\pi} \int \frac{dk}{2\pi} \sum_{k_\perp} G_R(E, \vec{k}) = \sum_{n=-N}^{N} \frac{1}{\pi v_n}\,. \tag{7}$$

Prefactors in expressions such as Eq. (7) are always chosen to ensure the correct 1D limit for $N = 0$. In the 2D limit, $N \gg 1$, the above DOS is related to the conventional 2D DOS, $\nu_{2D} = k_F/2\pi v$, via $\nu_0 = 2\pi R \nu_{2D}$. The vertex renormalization due to one impurity line is described by

$$\begin{aligned}\xi(\omega, \vec{q}) &= \frac{1}{\pi \nu_0 \tau} \int \frac{dk}{2\pi} \sum_{k_\perp} G_R(E + \omega, \vec{k} + \vec{q}) G_A(E, \vec{k}) \\ &= \sum_n \sum_{\sigma=\pm} \frac{1}{2\pi \nu_0 v_n} [1 - i\omega\tau + i\sigma v_n \tau (q + n q_\perp/\sqrt{(k_F R)^2 - n^2})]^{-1},\end{aligned} \tag{8}$$

where $q_\perp = m/R$ is also quantized. In the low-energy long-wavelength limit, $\omega\tau, |\vec{q}|\ell \ll 1$, Eq. (8) implies

$$\xi(\omega, \vec{q}) = 1 + i\omega\tau - Dq^2\tau - D_\perp q_\perp^2 \tau\,, \tag{9}$$

with diffusion constants $D = (\tau/\pi\nu_0)\sum_n v_n$ and

$$D_\perp = (\tau/\pi\nu_0)(v/k_F R)^2 \sum_n n^2/v_n \le D\,.$$

One checks easily that $D_\perp \to D$ for large $k_F R$, with $D \to v^2\tau/2$. For $N = 0$, however, $D_\perp = 0$ and $D = v^2\tau$, and therefore both 1D and 2D limits are correctly reproduced. Summing the usual ladder series then directly implies a diffusion pole, $[1 - \xi(\omega, \vec{q})]^{-1}$.

To ensure the validity of the ladder approximation, however, the smallness of "crossed" diagrams first needs to be checked. Since here one is actually in between the 1D and 2D limits, the usual reasoning leading to a suppression factor $1/k_F\ell$ for crossed diagrams does not apply. Evaluation of the simplest diagram of the crossed type and comparing it to the corresponding ladder diagram gives

a suppression factor $f = (1/2)\sum_n 1/(\pi\nu_0 v_n)^2$. Since $f = 1/2$ for $N = 0$, it is clearly not justified to neglect crossed diagrams for small doping level μ, where one approaches the 1D limit. The resulting breakdown of the diffusive picture in this limit is of course expected from 1D localization theory. For $k_F R \gg 1$, however, we obtain $f \simeq \ln(k_F R)/[2\pi^2 k_F R] \ll 1$, and are thus entitled to neglect crossed diagrams. In that case, $D_\perp \simeq D = v^2\tau/2$.

Here we consider an effectively short-ranged 1D interaction, $U(\vec{q}) \approx U_0$, since the $1/r$ tail of the Coulomb interaction potential is often externally screened, e.g., by close-by metallic gates. Even when working on an insulating substrate, a situation characterized by a long-ranged interaction, the finite length of the MWNT will lead to a cutoff for the logarithmic singularity. Note that U_0 represents a 1D Fourier component and hence is appropriate for screening lengths λ_s large compared to R. In the 2D limit, $R \gg \lambda_s$, this interaction constant is related to the respective 2D parameter via $U_0 = U_{2D}/R$. For the case of interest here, $R \ll \lambda_s$, and the order-of-magnitude estimate $U_0/2\pi v \approx 1$ follows [10], implying a dielectric constant $\epsilon \approx 10$. Under an extended Hubbard model description, this amounts to $U/t \approx 1$–5 in standard terminology. The first-order interaction correction to the TDOS can then be obtained following well-known arguments [12,18]. Since the Hartree correction is subleading, we focus on the exchange correction,

$$\frac{\delta\nu(E)}{\nu_0} = -\frac{\tau}{\pi}\,\mathrm{Re}\int\frac{dq}{2\pi}\sum_{q_\perp} U(\vec{q})\,\frac{\xi(E,\vec{q})}{1-\xi(E,\vec{q})}\,. \quad (10)$$

Together with Eq. (8), this result describes the complete crossover from the ballistic LL to the diffusive limit. For $\tau \to \infty$, no energy dependence is found, in agreement with $\alpha^{\mathrm{LL}} = 0$ to this order in U_0. In the diffusive limit, however, Eq. (10) can be simplified to

$$\frac{\delta\nu(E)}{\nu_0} = -\frac{U_0}{2\pi\sqrt{D}}\,\mathrm{Re}\sum_{n=-N}^{N}(-iE + Dn^2/R^2)^{-1/2}. \quad (11)$$

The $n = 0$ contribution yields the $E^{-1/2}$ 1D AAL correction, while the $n \neq 0$ contributions give a 2D logarithmic correction [12,18],

$$\delta\nu(E)/\nu_0 = \alpha\ln(E/E_0)\,, \quad (12)$$

with $E_0 \approx \mu$ and $\alpha = U_0 R/(2\pi D)$. Comparing the 1D and 2D contributions in Eq. (11), we see that only for sufficiently low-energy scales, $E < E^\star$, the 1D AAL law, $\delta\nu \sim E^{-1/2}$, takes over, where we estimate

$$E^\star \approx \frac{D}{(2\pi R)^2} \quad (13)$$

for the crossover scale. Equation (13) holds for weak-to-intermediate interactions, but may change for very strong interactions. For $E > E^\star$, Eq. (12) then gives the leading contribution, and the TDOS should be essentially equivalent to the one of a 2D disordered interacting metal.

Since in MWNTs the interactions are of intermediate strength, the lowest-order result (12) is not sufficient. Higher-order terms in U_0 were recently discussed by Kamenev and Andreev [19]. In the framework of the dynamical Keldysh formalism for a 2D system with long-ranged Coulomb interactions, a derivation of the TDOS valid for arbitrary interaction strength has been presented. Within the saddle-point approximation for the emerging nonlinear σ model, the electromagnetic modes are indeed Gaussian, with spectral density [19]

$$I(\omega) = \frac{\omega}{\pi}\,\mathrm{Im}\sum_{\vec{q}}\frac{1}{(Dq^2 - i\omega)^2} \times\left(U_0^{-1} + \frac{\nu_0 Dq^2}{Dq^2 - i\omega}\right)^{-1}. \quad (14)$$

Adopting this result to MWNTs in the energy regime $E > E^*$, the bulk exponent $\alpha = I(\omega \to 0)$ follows as

$$\alpha = \frac{U_0 R}{2\pi D}\,\frac{\ln(1+\nu_0 U_0)}{\nu_0 U_0}\,. \quad (15)$$

For weak interactions, the second factor is close to unity, and thus α is just the prefactor in Eq. (12). In effect, the AAL logarithmic correction therefore *exponentiates* into a power law. By using $U_0/2\pi v \approx 1$ and $N \approx 5$, we then estimate $\alpha \approx R/\ell$. To compare with experiment, note that $\ell \approx 10R$ from Eq. (4), as long as only intrinsic disorder via the inner-shell potentials is present. One then gets the same exponent for different tubes, $\alpha \approx 0.1$. When "true" disorder is included, α should increase and depend on the particular MWNT. This appears to be in qualitative agreement with Ref. [5], where values between $\alpha = 0.24$ and 0.37 were observed for 11 different MWNTs.

Next we turn to the *boundary TDOS* by considering a semi-infinite MWNT, $x \geq 0$. In the absence of disorder, the boundary Greens function is ($\delta = 0^+$),

$$G_0^b(E,k_\perp;x,x') = \int_0^\infty\frac{dk}{2\pi} \times\frac{4\sin(kx)\sin(kx')}{E+\mu-E(\vec{k})+i\delta\,\mathrm{sgn}(E)}\,,$$

which can be written as $G_0^h(x-x') - G_0^h(x+x')$ with the homogeneous Greens function G_0^h. Therefore the boundary simply causes the "image term" $-G_0^h(x+x')$. To include disorder, it is convenient to solve the Dyson equation in a real-space formalism. In the Born approximation, the self-energy is $\Sigma(x) = (\pi\nu_0\tau)^{-1}\times[G_0^h(0) - G_0^h(2x)]$. If we retain only the $G_0^h(0)$ term in the self-energy, the disorder-averaged boundary Greens function is

$$G^b(E,k_\perp;x,x') = \int_0^\infty\frac{dk}{2\pi}\,4\sin(kx)\sin(kx')G(E,\vec{k})\,, \quad (16)$$

where we use Eq. (6). In the 1D limit, $k_F R \lesssim 1$, the image part $-G_0^h(2x)$ in the self-energy is crucial and modifies the structure of G^b. For the more interesting limit $k_F R \gg 1$, it suffices to analyze a semi-infinite plane, with the

lowest-order correction from the image part

$$\delta G^b(\vec{r},X) = -\frac{1}{\pi\nu_{2D}\tau}\int d\vec{x}'' G_0^h\left(\frac{\vec{r}}{2}-\vec{x}''\right) \times G_0^h(2x''+2X,0)G_0^h\left(\frac{\vec{r}}{2}+\vec{x}''\right), \quad (17)$$

where the integration extends over the half plane, $X = (x + x')/2$ is the distance to the boundary, and $\vec{r} = \vec{x} - \vec{x}'$ is the relative coordinate. For $\vec{r} = 0$, this can be seen to vanish identically. Under the conditions that $k_F X \gg 1$ and $k_F r \gg 1$, Eq. (17) simplifies to

$$\delta G^b(\vec{r},X) \simeq -\frac{1}{k_F \ell \nu_{2D}} G_0^h(2X) G_0^h(r).$$

This gives subleading corrections to Eq. (16) that are suppressed by a factor $1/k_F X$ or $1/k_F r$, whichever is smaller. As these corrections die out on the microscopic length scale $1/k_F$, we take Eq. (16) in what follows.

The real-space diagrammatic perturbation theory can then be carried out explicitly. Dressing the interaction vertices with impurity lines within the ladder approximation, the first-order correction to the TDOS at position x in the diffusive limit is

$$\frac{\delta\nu(E,x)}{\nu_0} = -\frac{\tau}{\pi}\,\mathrm{Re}\int\frac{dq}{2\pi}\,2\cos^2(qx)\sum_{q_\perp}U(\vec{q}) \times \frac{\xi(E,\vec{q})}{1-\xi(E,\vec{q})},$$

with $\xi(E,\vec{q})$ given by Eq. (9). For $x \gg (D/E)^{1/2}$, we recover the bulk result (10). However, when tunneling into the end of the MWNT, $x \ll (D/E)^{1/2}$, the prefactor in Eq. (12) gets *doubled.* This doubling can be rationalized using the quasiclassical picture of Ref. [20], where the TDOS at position x is related to the Fourier transform of the return probability $P(x,t)$. The latter satisfies the diffusion equation with the boundary condition that no current flows across the boundary, leading to $P(x,t)/P(\infty,t) = 1 + \exp(-x^2/Dt)$. Close to the boundary, the return probability is then doubled.

Repeating the above arguments leading to the power law (1) for the bulk TDOS then implies again a power law, now characterized by the boundary exponent $\alpha_{\mathrm{end}} = 2\alpha$. The doubling of the exponent as one goes from the bulk to the boundary is in agreement with the experimental results of Ref. [5]. It should be noted that our derivation holds only in the diffusive limit. Remarkably, this doubling—which is based on the properties of the boundary diffuson close to the edge—coincides with the prediction of the classical resistor model.

Let us conclude by listing several open questions raised by our work. Future work needs to address the situation at small doping levels, the magnetic field dependence of the TDOS, and the conductivity. We hope that future theoretical and experimental works continue to reveal the subtle and beautiful interplay of disorder, dimensionality, and interactions presented by multiwall nanotubes.

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