Correlation Gap in Armchair Carbon Nanotubes

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We revisit the problem of the correlation gap in \((n, n)\) armchair carbon nanotubes, that would be metallic in the absence of electron-electron correlations. We attack the problem in the context of a Hubbard model with on-site repulsion \(U\) only, and we show that the scaling of the gap as \(\exp(-nt/U)\) predicted by Balents and Fisher (Phys. Rev. B 55, R11973 (1997)), can only be valid if \(U\) is not too large, even for very large values of \(n\). Using Hartree–Fock calculations and Renormalisation Group arguments we derive the scaling of the gap as a function of \(n\) for a given value of \(U\). Possible applications for the magnitude of the correlation gap in armchair carbon nanotubes will be discussed.

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I. INTRODUCTION

In the last few years exciting experiments have been done on single wall carbon nanotubes (SWCNT). It has been shown that SWCNT can behave as a true quantum wire showing coherent transport [1]. Luttinger–liquid behaviour was proposed [2] and there are indications for intrinsic superconductivity [3]. The typical dimensions of the CNT used in these experiments are a few nm for the diameter and several hundreds of nm for the length. Treating CNT in a single particle picture, the electronic properties depend strongly on chirality [4]. In particular armchair CNT are metallic and their Fermi surface at half–filling consists of two points only. At this so-called Fermi points, bands with nearly linear dispersion relations cross (Fig. 1). This property makes armchair CNT an ideal candidate for a one–dimensional quantum wire forming a Luttinger liquid [5].

In 1997 Balents and Fisher [6] considered the problem of the correlation gap in half–filled \((n, n)\) armchair carbon nanotubes. By excluding all but the lowest bands and using an on–site Hubbard interaction \(U\), they mapped the problem onto a two–chain Hubbard model with an effective interaction \(u_n = U/n\). For this model it is known from renormalisation group (RG) calculations (see [6] and references therein) that the functional dependence of the gap \(\Delta\) on \(u_n\) and \(t\) is given by

\[
\Delta \sim t \exp\left(-ct/u_n\right) \quad \text{if } u_n \ll t.
\]

In other words, \((n, n)\) armchair CNT at half–filling with large enough \(n\) are predicted to be metallic for practical purposes since the correlation gap is exponentially small.

In this paper we argue that the scaling law in Eqs. (1) can only be valid, even for large \(n\), if at the same time the interaction strength \(U\) is not too large. This can already be seen from the 2D limit, i.e. when \(n\) approaches infinity. In this limit we expect a metal–insulator transition at some critical value \(U_{cr}\) of the interaction strength [7, 8]. Even at finite \(n\) the gap will be exponentially small only up to \(U_{cr}\) but will grow linearly for larger values of \(U\). In the following we derive the scaling law of the gap as a function of \(n\) and \(U\). This gap is determined from Hartree–Fock (H–F) calculations where we take into account all the bands. We expect from the H–F method that it produces the correct functional dependence in the exponent of the correlation gap. This is the case for the Hubbard model in one dimension where the Bethe Ansatz solution is reproduced up to a prefactor [9]. On qualitative grounds we show how we can get this scaling law from a RG argument.

II. THE CORRELATION GAP FROM H–F CALCULATIONS

We are going to think about a SWCNT as a rectangular graphite monolayer rolled up into a cylinder. This is equivalent to considering a rectangular honeycomb lattice (Fig. 2) with the appropriate periodic boundary conditions. All the SWCNT can be classified by their chirality vector \(C_h = na_1 + ma_2\), where \(a_1\) and \(a_2\) are the basis vector of the honeycomb lattice, while \(n\) and \(m\) are integers with \(m < n\) [4]. \(C_h\) determines into which

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{bands.png}
\caption{The energy bands near the Fermi level for armchair CNT at half–filling.}
\end{figure}
direction the graphene layer is rolled up. As discussed in the introduction, the armchair CNT are of particular interest since at half-filling they are always metallic in the non-interacting electron approximation (see Fig. 1). Armchair CNT are characterized by chiral vectors of the form \( \mathbf{C}_h = n\mathbf{a}_1 + n\mathbf{a}_2 \), i.e. \( n = m \). An example is shown in Fig. 2. In our calculations we take the tubes to be very long and we use also periodic boundary conditions at the ends of the tube. To determine the charge gap in \((n, n)\) armchair nanotubes, we consider the following model with nearest neighbor hopping and on-site Hubbard interaction at half-filling:

\[
H = \sum_{\langle i,j \rangle} \left( t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \text{h.c.} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \lambda \sum_{\langle i,j \rangle} \left( n_{i\uparrow} \langle n_{i\downarrow} \rangle + \langle n_{i\downarrow} \rangle n_{i\uparrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \right)
\]

\( \sigma \) is the spin index and \( i,j \) sum over the sites of a rectangular armchair-type honeycomb lattice with periodic boundary conditions. \( c^\dagger_{i\sigma} \) are the fermion creation operators and \( n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma} \). The hopping integrals \( t_{ij} \) are restricted to nearest neighbors and are taken to be equal to a single \( t \) for all the hoppings. In the case of half-filling and on bipartite lattices with non-frustrated hopping, the H–F Hamiltonian is [3]

\[
H = \sum_{\langle i,j \rangle} t_{ij} c^\dagger_{i\sigma} c_{j\sigma} + \text{h.c.} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \lambda \sum_{\langle i,j \rangle} \left( n_{i\uparrow} \langle n_{i\downarrow} \rangle + \langle n_{i\downarrow} \rangle n_{i\uparrow} - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \right)
\]

with the expectation values given by

\[
\langle n_{i\sigma} \rangle = 1/2 \left( 1 + m(-1)^{\lambda_{i\sigma}} \right)
\]

where \( \lambda_{i\sigma} = 1, \lambda_{\sigma,-\sigma} = -1 \) and \( m = |\langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle| \). This Hamiltonian can be diagonalized by a Bogoliubov transformation and it yields the self-consistent H–F equation for the sublattice magnetisation:

\[
m = \frac{2}{N} \sum_{k \in 1^{st}BZ} \frac{U m}{\sqrt{U^2 m^2 + 4\epsilon^2(k)}}
\]

\( N \) is the total number of sites and \( \epsilon(k) \) is the tight binding dispersion relation for a single graphite layer given by:

\[
\epsilon^2(k) = 3t^2 + 2t^2 \left[ \cos(k \cdot \mathbf{a}_1) + \cos(k \cdot \mathbf{a}_2) \right] + \cos(k \cdot (\mathbf{a}_1 - \mathbf{a}_2))
\]

Finally the gap is obtained from the sublattice magnetisation:

\[
\Delta = \min_k \sqrt{U^2 m^2 + 4\epsilon^2(k)} = Um
\]

In Fig. 3 the numerical results for the correlation gap are shown. We have two parameters to vary, the tube diameter which is proportional to \( n \) and the interaction strength \( U \). We tried to fit the H–F results to
\[ cU/t \exp(-\lambda t/U) \] when we varied \( U \) and to \( c \exp(-\lambda n) \) for a variation of \( n \). We see that these fits break down at a critical value of the interaction strength \( U^{HF}_{cr} = 2.23t \).

There is no exponential decay beyond \( U^{HF}_{cr} \). In particular for \( U = U^{HF}_{cr} \) we can fit the data to \( c/n \), a power law. All our calculations can be summarized in the following scaling law

\[ \Delta/t = 1/n \exp \{-\alpha n(t/U - t/U^{HF}_{cr})\} \]  

with \( \alpha = 5.44 \). \( U^{HF}_{cr} \) is identical to the critical value in the H–F approximation to open a gap in the two-dimensional honeycomb lattice. We see that if \( U \) is approaching \( U^{HF}_{cr} \) the exponent is going to vanish and we are left with a power law \( \Delta = t/n \).

### III. RG–ARGUMENT

To compute the charge gap from a RG–calculation we need to compute the RG–equation up to third order in \( U \) and we denote by \( \tilde{g} \) the effective coupling constant corresponding to the momentum cutoff \( \tilde{D} \). The third order equation is

\[ \frac{d \tilde{g}}{d \ln \tilde{D}} = -\frac{1}{\pi v_c} \tilde{g}^2 + \frac{1}{2\pi^2 v_c^2} \tilde{g}^3 \]  

with \( v_c = v_F + U/(2\pi n) \). The RG flow has to be stopped at the strong coupling region. This should occur when the momentum cutoff \( \tilde{D} \) corresponds to the energy scale of the charge gap \( \Delta_c \). The flow of the running coupling constant has to be stopped at the first relevant energy scale. In the usual one–band picture this energy scale is just the kinetic energy \( \sim t \). But in the present problem there is another energy scale entering before: It is the gap to the next band which is of order \( t/n \). This argument leads to \( \tilde{g}(\Delta_c) \sim t/n \). Now we can integrate out the degrees of freedom far from the Fermi level, and we get

\[ \int_{\Delta_c/v_c}^{\tilde{D}_0} d(\ln \tilde{D}) = -\int_{\tilde{g}(\Delta_c)}^{g} d\tilde{g} \left( \frac{\tilde{g}^2}{\pi v_c} \left( 1 - \frac{\tilde{g}}{2\pi v_c} \right) \right)^{-1} \]  

where \( \tilde{D}_0 \) is the initial cutoff with \( \tilde{g}(\tilde{D}_0) = g = U/n \). To leading order in \( g \) and \( \tilde{g}(\Delta_c) \) we obtain

\[ \ln \left( \frac{\Delta_c/v_c}{\tilde{D}_0} \right) \sim -\beta t \frac{\Delta_c}{\tilde{g}(\Delta_c)} + \frac{t}{\tilde{g}(\Delta_c)} \]  

Identifying the relevant energy scales we can write the charge gap as

\[ \Delta_c \sim \exp(-\beta t/(U/n) + \gamma n) \]  

We note that this argument leads to the H–F result.

### IV. DISCUSSION

Fig. 4 summarizes our results obtained from H–F calculations and the RG argument on the correlation gap in armchair CNT. We observed that there is an exponentially small gap only if \( U \ll U^{HF}_{cr} \), even for large \( n \). \( U^{HF}_{cr} \) is a critical value for the interaction strength. For values \( U < U^{HF}_{cr} \) the correlation gap follows an exponential scaling law. For \( U > U^{HF}_{cr} \) the gap is growing linearly. The actual value of the hopping integral \( t \) in SWCNT is about 2.4 eV \[12\]. This value is large and as a consequence we observe in the case \( U \lesssim U^{HF}_{cr} \) a finite gap which is of order meV. As an example we look at a \((10,10)\) CNT assuming an interaction strength of \( U = 2t \). In this case we obtain for the gap a value of 0.006meV which corresponds to an energy of 14 meV and a temperature of 160 K. For smaller CNT the gap is even larger.

These results are based on two approximations, namely the description of electron-electron interactions in terms of a Hubbard model with only on-site repulsion, and the calculation of the gap within Hartree-Fock theory. Let us now critically review these approximations.

**Hubbard model**: It is by now well accepted that metallic nanotubes behave as Luttinger liquids with an exponent controlled by the long-range tail of the Coulomb repulsion and by the finite length of the tube \[13\]. However, when it comes to calculating the correlation gap in half-filled systems, the short-range part of the correlations plays a dominant role. This is most easily seen in the atomic limit where the hopping integrals are assumed to be vanishingly small. So let us assume for a moment that the system is described by the Hamiltonian:

\[ H = U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{\langle i,j \rangle} V_{ij} n_i n_j \]  

where \( n_i = n_{i\uparrow} + n_{i\downarrow} \) is the total density, and where \( V_{ij} \) is the long-range part of the repulsion that does not need
to be specified. According to Mott’s prescription to evaluate the gap [13], one has to compare the energy of a uniform configuration with that of a configuration with a doubly occupied site and a hole far apart from each other. The only difference comes from the energy of the electron that has been moved, and the energy increase is precisely equal to $U$ since it still interacts with further neighbours in the same way. So, even in the presence of long-range Coulomb repulsion, the value of the charge gap is controlled by the on-site repulsion $U$ in the atomic limit. Of course, away from the atomic limit, the long-range part of the Coulomb interaction will play a role. To get a quantitative estimate of the charge gap in that case is a very difficult problem though which has not been solved even in the simplest case of a pure one-dimensional model, but if anything the longer range part of the Coulomb repulsion is expected to reinforce the tendency to localize the charge, hence to increase the charge gap. So to use a simple Hubbard model with only on-site repulsion to calculate the correlation gap of a half-filled system is a reasonable assumption, and the value is probably an underestimate of the actual gap in the presence of the long-range part of the Coulomb repulsion. For the present purpose this is all we need since our main conclusion is to argue that the gap might be larger than previously assumed.

**Hartree-Fock approximation:** In purely one-dimensional systems, Hartree-Fock is known to reproduce correctly the exponential form of the gap as a function of $U$, but the prefactor of the exponential is wrong, and the gap is overestimated by a factor $\sqrt{t/U}$. This is only a problem for very small values of $U/t$, but in the range of interest to us, namely not too far from $U_{cr}$, this is not a problem any more. In two dimensions, very little is known precisely regarding the value of the correlation gap for models without perfect nesting. Luckily enough, the Hubbard model on the honeycomb lattice has been extensively studied by Monte Carlo simulations, and although the gap could not be calculated, the critical value $U_{cr}$ has been determined by looking at the development of magnetic long-range order [3, 4] and the value is around $U_{cr} = 3.6t$. This is clearly larger than the Hartree-Fock result $U_{HF}^{\text{cr}} = 2.23t$, but the order of magnitude is the same. Since the gap is anyway expected to grow linearly with $U$ beyond the critical value, the main result of Hartree-Fock that the gap in the nanotube geometry could take large values if $U$ is not too far below $U_{cr}$ is expected to remain true beyond Hartree-Fock.

The relevance of this calculation depends crucially on the actual value of $U$ in nanotubes. What we need here is the atomic value for carbon. The fact that graphite, a system of very weakly coupled honeycomb planes, is a semi-metal and not an insulator just tells us that $U$ does not exceed $U_{cr}$. Besides, values often quoted for fullerenes are of no help since they concern the molecule $C_{60}$ and not the atomic value for carbon. The most relevant value which we could find in the literature was for polyacetylene where an on-site repulsion of 5–10 eV is generally used [4]. So we believe that values in the range of 2$t$ to 4$t$ are to be expected. In particular, a value of $U$ near the critical one seems plausible. Thus if in real CNT $U \lesssim U_{cr}$, a correlation gap of a few meV has to be present and a gap of such magnitude could in principle be observed experimentally.

This of course will only be true for SWCNT at half-filling. Currently available CNT seem to have some self-doping which shifts the Fermi–level to an energy where several bands are cut. This turns the CNT metallic independently of their chirality. There are ongoing experimental efforts however identifying the nature of the doping and producing undoped samples, and we are confident that it will be soon be possible to test the conclusions of the present work.

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