Quasi-Phase Transition and Many-Spin Kondo Effects in Graphene Nanodisk

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The trigonal zigzag nanodisk with size $N$ has $N$ localized spins. We investigate its thermodynamical properties with and without external leads. Leads are made of zigzag graphene nanoribbons or ordinary metallic wires. There exists a quasi-phase transition between the quasi-ferromagnet and quasi-paramagnet states, as signaled by a sharp peak in the specific heat and in the susceptibility. Lead effects are described by the many-spin Kondo Hamiltonian. A new peak emerges in the specific heat. Furthermore, the bandwidth of free electrons in metallic leads becomes narrower. By investigating the spin-spin correlation it is argued that free electrons in the lead form spin-singlets with electrons in the nanodisk. They are indications of many-spin Kondo effects.

Introduction: Graphene nanostructure\(^1\) has the potential for future application in nanoelectronics and spintronics. In particular, much attention is now focused on graphene nanoribbons\(^2\) due to almost flat low-energy band at the Fermi level depending on the edge states. Another basic element of graphene derivatives is a graphene nanodisk\(^3, 4, 5, 6, 7, 8\). It is a nanometer-scale disk-like material which has a closed edge. There are many type of nanodisks, among which the trigonal zigzag nanodisk is prominent in its electronic and magnetic properties because there exist $N$-fold degenerated zero-energy states when its size is $N$ (Fig.1).

In this paper we explore thermodynamical properties of the trigonal zigzag nanodisk. The system is well approximated by the infinite-range Heisenberg model. It is exactly solvable. A sharp peak emerges in the specific heat and in the susceptibility, which we interpret as a quasi-phase transition between the quasi-ferromagnet and quasi-paramagnet states. We then investigate a nanodisk-lead system, where the lead is made of a zigzag graphene nanoribbon or an ordinary metallic wire. We refer to it as a graphene lead or a metallic lead.

It is shown that lead effects are described by the many-spin Kondo Hamiltonian. Electron spins in the nanodisk and the lead orient into the opposite directions to lower the coupling energy. A new peak appears around a certain temperature ($T = T_K$) in the specific heat but not in the susceptibility for small size nanodisks. The internal energy decreases near the peak, and the band width of free electrons in the lead becomes narrower in the instance of the metallic lead. Furthermore, the spin-spin correlation takes the maximum value at $T = 0$, remains almost constant for $T \lesssim T_K$, and then decreases monotonically as $T$ increases. We interpret these phenomena to mean that free electrons in the lead are consumed to make spin-singlets with electrons in the nanodisk. It is intriguing that all electrons (only a few portion of electrons) in the nanodisk are engaged in the case of the graphene (metallic) lead. They are indications of Kondo effects due to the Kondo coupling between electrons in the lead and the nanodisk.

![Graphene nanodisk](image)

**Fig. 1:** (a) Trigonal zigzag nanodisks. The size parameter $N$ is defined in this way. The number of carbon atoms is given by $N_C = N^2 + 6N + 6$. (b) The nanodisk-lead system. The nanodisk with $N = 7$ is connected to the right and left leads.

**Quasi-Ferromagnet:** The size-$N$ zigzag trigonal nanodisk has $N$-fold degenerated zero-energy states\(^4\), where the gap energy is as large as a few eV. Hence it is a good approximation to investigate the electron-electron interaction physics only in the zero-energy sector, by projecting the system to the subspace made of those zero-energy states. The zero-energy sector consists of $N$ orthonormal states $|f_\alpha\rangle$, $\alpha = 1, 2, \cdots, N$, together with the SU(N) symmetry. Let $U_{\alpha\beta}$ and $J_{\alpha\beta}$ be the Coulomb energy and the exchange energy between electrons in the states $|f_\alpha\rangle$ and $|f_\beta\rangle$. It follows\(^7\) that $J_{\alpha\beta} \approx U_{\alpha\beta}$ and that all $J_{\alpha\beta}$ are of the same order of magnitude for any pair of $\alpha$ and $\beta$, implying that the SU(N) symmetry is broken but not so strongly. It is a good approximation to start with the exact SU(N) symmetry, by replacing $U_{\alpha\beta}$ and $J_{\alpha\beta}$ with their averages $U$ and $J$, respectively. Then, the zero-energy sector is described by the Hamiltonian\(^9\),

$$H_D = -JS_{\text{tot}}^2 + \frac{1}{2}U'n_{\text{tot}}^2 + \left(\frac{U}{2} + J\right)n_{\text{tot}},$$

with $U' \equiv U - \frac{1}{2}J$ and $J \approx U$, where $S_{\text{tot}} = \sum_\alpha S(\alpha)$ is the total spin, and $n_{\text{tot}} = \sum_\alpha n(\alpha)$ is the total electron number. Here, $n(\alpha) = d_{\alpha}^\dagger d_{\alpha}$ is the total electron number. Here, $n(\alpha) = d_{\alpha}^\dagger d_{\alpha}$ is the total electron number. Here, $n(\alpha) = d_{\alpha}^\dagger d_{\alpha}$ is the total electron number. Here, $n(\alpha) = d_{\alpha}^\dagger d_{\alpha}$ is the total electron number. Here, $n(\alpha) = d_{\alpha}^\dagger d_{\alpha}$ is the total electron number. Here, $n(\alpha) = d_{\alpha}^\dagger d_{\alpha}$ is the total electron number. Here, $n(\alpha) = d_{\alpha}^\dagger d_{\alpha}$ is the total electron number. Here, $n(\alpha) = d_{\alpha}^\dagger d_{\alpha}$ is the total electron number. Here, $n(\alpha) = d_{\alpha}^\dagger d_{\alpha}$ is the total electron number.

Apart from an irrelevant constant, the Hamiltonian\(^11\) is the infinite-range Heisenberg model, $H_S = -JS_{\text{tot}}^2$, in the half-filled sector with $n_{\text{tot}} = N$. The nanodisk spin
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The nanodisk spin system exhibits a strong ferromagnetic order due to a large exchange interaction. The relaxation time is finite but quite large even if the size \( N \) is small. We have called such a system quasi-ferromagnet [4].

**Thermodynamical Properties:** The infinite-range Heisenberg model is exactly diagonalizable, \( H_S|\Psi_S\rangle = E_S|\Psi_S\rangle \), with \( E_S = -JS(S + 1) \), where \( S \) takes half-integer or integer values from \( N/2 \) down to 1/2 or 0, depending on whether \( N \) is odd or even. The total degeneracy of the energy level \( E_S \) is \((2S + 1)g_N(S)\) with \( g_N(N/2 - q) = N! C_q - N! C_{q - 1} \).

We have a complete set of the eigenenergies together with their degeneracies. The partition function of the nanodisk with size \( N \) is exactly calculable,

\[
Z_S = \sum_S (2S + 1)g_N(S)e^{-\beta JS(S + 1)}. \tag{2}
\]

According to the standard procedure we can evaluate the specific heat \( C_N(T) \), the entropy \( S_N(T) \), the magnetization \( \langle S_{tot}^z \rangle \) and the susceptibility \( \chi = \frac{1}{\beta h^2} \left( \langle S_{tot}^2 \rangle - \langle S_{tot}^z \rangle^2 \right) \) from this partition function. The entropy is given by \( S_N(0) = k_B \log(N + 1) \) at zero temperature, corresponding to the ground state multiplicity \( N + 1 \). We display them in Fig. 2 for size \( N = 1, 2, 2^2, \cdots 2^{10} \).

There appear singularities in thermodynamical quantities as \( N \rightarrow \infty \), which represent a phase transition at \( T_c \). For finite \( N \), there are steep changes around \( T_c \), though they are not singularities. It is not a phase transition. However, it would be reasonable to call it a quasi-phase transition between the quasi-ferromagnet and quasi-paramagnet states. Such a quasi-phase transition is manifest even in finite systems with \( N = 100 \sim 1000 \).

The specific heat and the magnetization take non-zero values for \( T > T_c \) [Fig. 2(a), (c)], which is zero in the limit \( N \rightarrow \infty \). The entropy for \( T > T_c \) is lower than that of the paramagnet [Fig. 2(b)]. These results mean the existence of some correlations in the quasi-paramagnet state. The maximum value of the susceptibility increases linearly as \( N \) becomes large. It is an indicator of the quasi-phase transition.

**Many-Spin Kondo Hamiltonian:** We proceed to investigate how thermodynamical properties of the nanodisk is affected by the attachment of the leads. Though there are two leads attached to a nanodisk, the lead Hamiltonian \( H_L \) and the transfer Hamiltonian \( H_T \) are expressed as if there were a single lead after a certain transformation [7],

\[
H_L = \sum_{k\sigma} \varepsilon(k)c_{k\sigma}^\dagger c_{k\sigma}, \tag{3a}
\]

\[
H_T = i\sum_{k\sigma} \sum_\alpha \left( c_{k\sigma}^\dagger d_{\sigma}(\alpha) + d_\alpha^\dagger (\alpha)c_{k\sigma} \right), \tag{3b}
\]

where \( c_{k\sigma} \) is the annihilation operator of electron in the lead with the wave number \( k \) and the dispersion relation \( \varepsilon(k) \).

When charges transfer between the nanodisk and the leads, the total electron number \( n_{tot} \) is no longer fixed in the nanodisk. However, the nanodisk remains to be half-filled, when a charge transfers from the lead to the nanodisk and then transfers back from the nanodisk to the lead. The process is the second order effect in the tunneling coupling constant \( \tilde{t} \). We derive the effective Hamiltonian for such a process.

The total Hamiltonian is \( H = H_D + H_L + H_T \). We take \( H_0 = H_D + H_L \) as the unperturbed term and \( H_T \) as the perturbation term. Note that \( U \gg \tilde{t} \). We make a canonical transformation known as the Schrieffer-Wolff transformation [10] to eliminate \( H_T \),

\[
H \rightarrow \tilde{H} = e^{iG}He^{-iG},
\]

with \( G = \frac{1}{2}[G, H_0] = 0 \). The dominant contribution comes from the Fermi surface, \( \varepsilon(k) = \varepsilon_F \). We assume the symmetric condition \( \varepsilon_F = U + \frac{1}{2}U' \) with respect to the Fermi energy. Then, after a straightforward calculation, we obtain \( \tilde{H} = H_D + H_L + H_K + O(\tilde{t}^2) \), where \( H_K \) is the second order term in \( \tilde{t} \). It is the many-spin Kondo Hamiltonian,

\[
H_K = J_K \sum_{\mathbf{k}, \mathbf{k}', \sigma, \sigma'} c_{\mathbf{k}\sigma}^\dagger \tau_{\sigma\sigma'} c_{\mathbf{k}'\sigma'} \cdot S_{tot}, \tag{4}
\]

with the Kondo coupling constant \( J_K = 8\tilde{t}^2/U' \). The difference between the above many-spin Kondo Hamiltonian and the ordinary Kondo Hamiltonian is whether the local spin is given by the summation over many spins \( S_{tot} \) or a single spin \( S \). Note that \( S_{tot}^z \) is a dynamical variable but \( S^2 \) is not, \( S^2 = 3/4 \).
with the functional integration we find $Z$ freedom in a functional integral over the lead electron’s degree of freedom in (5).

$$ \psi = (c_1, c_1) \eta. $$

The partition function in the Matsubara form is given in terms of the Hamiltonian density $\mathcal{H}_{\text{eff}}$ as

$$ Z = \text{Tr}_S \int D\psi D\psi^\dagger \exp \left[ -\int_0^\beta d\tau \int dx \left( \psi^\dagger \partial_\tau \psi + \mathcal{H}_{\text{eff}} \right) \right] \quad \text{Tr}_S \left[ \exp (-\beta H_S) Z_K \right], $$

with $Z_K = \int D\psi D\psi^\dagger \exp [-S_K]$, where $Z_K$ is the action $S_K = \int_0^\beta d\tau \int dx \left( \psi^\dagger \partial_\tau \psi + \mathcal{H}_t + \mathcal{H}_K \right)$. We first perform a functional integral over the lead electron’s degree of freedom in $Z_K$, and then summed up the nanodisk spin in $[5]$. Because an electron in the lead is constrained within a very narrow region, it is a good approximation to neglect momentum scatterings,

$$ H_K \simeq 2J_K s \cdot S_{\text{tot}}, $$

where $s = \frac{1}{2} \sum_{k\sigma} c^\dagger_{k\sigma} \tau_{\sigma\sigma'} c_{k\sigma'}$ is the electron spin in the lead. The action $S_K$ is summarized as

$$ S_K = \int \frac{d\omega}{2\pi} \sum_{k} \psi^\dagger (k) M (k) \psi (k), $$

with $M (k) = -|\omega - \varepsilon (k)| + J_K \tau \cdot S_{\text{tot}}$. Performing the functional integration we find $Z_K = \text{Det}[M] = \exp [-\beta F_K]$, where $F_K$ is the Helmholtz free energy,

$$ F_K = \frac{1}{2\beta} \sum_k \ln \left[ \cosh (\beta J_K |S_{\text{tot}}|) + \cosh (\beta \varepsilon (k)) \right]. $$

This is reduced to the well-known formula for free electrons with the dispersion relation $\varepsilon (k)$ for $J_K = 0$.

**Functional Integration:** The total Hamiltonian is now given by $H_{\text{tot}} = H_S + H_t + H_K$ at half filling. We define the spinor $\psi = (c_1, c_1) \eta$. The partition function in the Matsubara form is given in terms of the Hamiltonian density $\mathcal{H}_{\text{eff}}$ as

$$ Z = \text{Tr}_S \int D\psi D\psi^\dagger \exp \left[ -\int_0^\beta d\tau \int dx \left( \psi^\dagger \partial_\tau \psi + \mathcal{H}_{\text{eff}} \right) \right] \quad \text{Tr}_S \left[ \exp (-\beta H_S) Z_K \right], $$

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This is reduced to the well-known formula for free electrons with the dispersion relation $\varepsilon (k)$ for $J_K = 0$.

**Zigzag Graphene Nanoribbon Leads:** We first consider the system where the leads are made of zigzag graphene nanoribbons. Owing to the flat band at the zero energy, $\varepsilon (k) = 0$, the result of the functional integration (8) is quite simple,

$$ F_K = -\frac{1}{\beta} \ln \cosh (\beta J_K |S_{\text{tot}}| /2). $$

The effective Hamiltonian for the nanodisk spin is $H_S + F_K$. The lead effect is to make the effective spin stiffness larger and the ferromagnet more rigid.

The trace over the nanodisk spin is carried out in (9),

$$ Z = \sum_S (2S + 1) g_N (S) e^{-\beta JS(S+1)} \cosh \left( \frac{\beta J_K}{2} \sqrt{S(S+1)} \right). $$

We compare thermodynamical properties of the nanodisk with leads (Fig.4) and without leads (Fig.2). The magnetization $S$ and the susceptibility $\chi$ are found to be indistinguishable from those of the nanodisk without leads (Fig.2). In Fig.3 we show the specific heat $C_G (T)$ and the entropy $S_G (T)$ for various size $N$. The significant feature is the appearance of a new peak in the specific heat at $T = T_K \approx (J_K / 2J)T_c$, though it disappears for large $N$. We examine the internal energy $E_G (T)$, which is found to decrease around $T_K$ (Fig.4). Near zero temperature it reads

$$ E_G (T) \simeq -JS_g^2 - \frac{J_K}{2} S_g + J_K S_g e^{-\beta J_K S_g}. $$

The first term ($\propto J$) represents the energy stabilization due to the ferromagnetic order present in the nanodisk without leads, while the second term ($\propto J_K$) represents the one due to the Kondo coupling. Furthermore, it follows that the entropy is reduced at zero temperature as $S_G (0) - S_N (0) = -k_B \log 2$, as implies that the ground state multiplicity at the zero temperature is just one half of that of the system without leads.

The spin-spin correlation $\langle |s \cdot S_{\text{tot}}| \rangle$ is calculated based on the partition function (10) and shown in Fig.3(a). Near zero temperature we find

$$ \langle |s \cdot S_{\text{tot}}| \rangle \simeq \frac{1}{2} S_g \tanh (\beta J_K S_g /2). $$

It takes the maximum value $S_g /2$ at $T = 0$, and remains almost constant for $T \lesssim T_K$, and then monotonically decreases as $T$ increases. Finally, it almost vanishes in the quasi-paramagnet phase for large $N$ since $\langle S_{\text{tot}} \rangle \approx 0$. We may interpret these phenomena as follows. Electrons in the lead and the nanodisk form spin-singlet states to lower the coupling energy (6). The singlet state is rather tight for $T \lesssim T_K$, but thermally broken as $T$ increases.

All these features indicate the occurrence of the Kondo effect due to the coupling between the spins in the nanodisk and the leads.
leads. In Fig.3, we show the specific heat holds for the entropy precisely as in the case of graphene entropy $S(T)$, the specific heat $C_M(T)$ and the internal energy $E_M(T)$ read as follows,

$$S_M(T) \simeq k_B \log \frac{N + 1}{2} + \frac{\pi^2}{3}\rho k_BT, \quad C_M(T) \simeq \frac{\pi^2}{6}\rho k_BT,$$

and $E_M(T) = E_G(T) + \Delta E(T)$ with

$$\Delta E(T) \simeq -\frac{\rho}{2} (D - JK_S)^2 + \frac{\pi^2}{6}\rho (k_BT)^2.$$

All terms proportional to $\rho$ have arisen from free electrons in the metallic lead. The internal energy $E_M(T)$ consists of two terms: $E_G(T)$ is identical to the energy for the nanodisk with graphene leads, and $\Delta E(T)$ is the energy of the metallic lead. The first term of $\Delta E(T)$ shows that the band width of free electrons in the lead becomes narrower due to the Kondo coupling. We may interpret that $n$ free electrons with

$$n = \rho J_K S_g$$

are consumed to make spin-coupling with electrons in the nanodisk. The second term is the thermal energy of free electrons in the metallic lead.

We show the spin-spin correlation $\langle |\langle s | S_{\text{tot}} \rangle| \rangle$ in Fig.5(b). The overall features are the same as for the nanodisk with graphene leads. However, there are new features. First of all, the value of correlation is quite small. This is because spin-singlets are formed only by a small portion of electrons in the metallic lead which are near the Fermi level. We expect that this number density is given by [17]. Indeed, it is observed that $\langle |\langle s | S_{\text{tot}} \rangle| \rangle \rightarrow \frac{1}{2}\rho J_K S_g$ at $T = 0$ as $N \rightarrow \infty$ [Fig.5(b)].

In this paper we have investigated thermodynamical properties of a zigzag graphene nanodisk without and with leads. The lead effects are summarized by the many-spin Kondo Hamiltonian. One effect is to enhance the ferromagnetic order. This result is important to manufacture spintronic circuits by connecting leads in nanodevices[9]. We have shown various thermodynamical results indicating many-spin Kondo effects.

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