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Quasiphase transition and many-spin Kondo effects in a 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 quasiphase transition between the quasiferromagnet and quasiparamagnet 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. An additional 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.

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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.[3–8] It is a nanometer-scale disklike material that has a closed edge. There are many types of nanodisks, among which the trigonal zigzag nanodisk is prominent in its electronic and magnetic properties because there exist N-fold degenerate half-filled zero-energy states when its size is N (Fig. 1). Spins make a ferromagnetic order, and the relaxation time is finite but quite large even if the size N is very small.[4] Furthermore, a nanodisk behaves as if it were a quantum dot with an internal degree of freedom, where the conductance exhibits a peculiar series of Coulomb blockade peaks.[7]

It has been pointed out[9] that one of the difficulties of realizing spintronics is the short spin-correlation length in low-dimensional graphene systems. It is important to make a detailed analysis of thermodynamical properties of the nanodisk spin system and how they are affected by the existence of the leads for future application. It is also interesting to examine how they depend on the lead whether it is made of a zigzag graphene nanoribbon or an ordinary metallic wire. (We refer to it as a graphene lead or a metallic lead.) Another important problem is the spin-dependent transport phenomenon. In particular we expect Kondo effects due to the Kondo coupling between electrons in the lead and the nanodisk.

In this Rapid Communication we explore thermodynamical properties of the trigonal zigzag nanodisk. A sharp peak emerges at a certain temperature ($T=T_c$) in the specific heat and in the susceptibility, which we interpret as a quasiphase transition between the quasiferromagnet and quasiparamagnet states. We then investigate a nanodisk-lead system. An additional peak appears around a certain temperature ($T=T_K$) in the specific heat but not in the susceptibility for small size nanodisks. By investigating the spin-spin correlation, we interpret it as an indication of many-spin Kondo effects. With respect to the ferromagnetic order, the lead effect is found to enhance it.

The size-N zigzag trigonal nanodisk has N-fold degenerate 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 $|f_\alpha\rangle$, $\alpha=1,2,\ldots,N$, 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 α and β, 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. The energy U and J is on the order of 0.1 eV.[7,9] Then, the zero-energy sector is described by the Hamiltonian,[10]

$$H_{\mathrm{D}} = -JS_{\mathrm{tot}}^2 + \frac{1}{2}U' n_{\mathrm{tot}}^2 + \left(\frac{U}{2}+J\right)n_{\mathrm{tot}}, \tag{1}$$

with $U' \equiv U - \frac{1}{2}J$ and $J \approx U$, where $\boldsymbol{S}_{\mathrm{tot}}=\Sigma_\alpha \boldsymbol{S}(\alpha)$ is the total spin and $n_{\mathrm{tot}}=\Sigma_\alpha n(\alpha)$ is the total electron number. Here, $n(\alpha)=d_\sigma^\dagger(\alpha)d_\sigma(\alpha)$ and $\boldsymbol{S}(\alpha)=\frac{1}{2}d_\sigma^\dagger(\alpha)\boldsymbol{\tau}_{\sigma\sigma'}d_{\sigma'}(\alpha)$ with $d_\sigma(\alpha)$ being the annihilation operator of electron with spin $\sigma=\uparrow,\downarrow$ in the state $|f_\alpha\rangle$: $\boldsymbol{\tau}$ is the Pauli matrix. We call $\boldsymbol{S}_{\mathrm{tot}}$ the nanodisk spin.

Apart from an irrelevant constant, Hamiltonian (1) is the infinite-range Heisenberg model, $H_S=-JS_{\mathrm{tot}}^2$, in the half-filled sector with $n_{\mathrm{tot}}=N$. The nanodisk spin takes the maximum value $S_g=\sqrt{N/2(N/2+1)}$ in the ground state, where all spins are spontaneously polarized. 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 quasiferromagnet.[4]

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 $(2S+1)g_N(S)$, where $g_N(N/2-q)={}_NC_q-{}_NC_{q-1}$ with the binomial coefficient ${}_NC_q=N!/[q!(N-q)!]$.

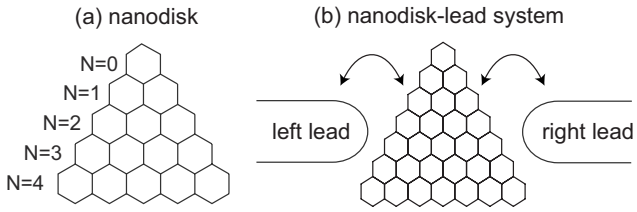

FIG. 1. (a) Trigonal zigzag nanodisks. The size parameter N is defined in this way. The number of carbon atoms is given by $N_C = N^2+6N+6$. (b) The nanodisk-lead system. The nanodisk with $N=7$ is connected to the right and left leads.

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 $C(T)$, the entropy $S(T)$, the magnetization $\langle \boldsymbol{S}_{\rm tot}^2 \rangle$, and the susceptibility $\chi = \frac{1}{k_B T}(\langle \boldsymbol{S}_{\rm tot}^2 \rangle - \langle \boldsymbol{S}_{\rm tot} \rangle^2)$ from this partition function. The entropy is given by $S(0) = k_B \log(N+1)$ at zero temperature, corresponding to the ground-state multiplicity $N+1$. We display them in Fig. 2 for size $N = 1, 2, 2^2, \ldots, 2^{10}$.

There appear singularities in thermodynamical quantities as $N \to \infty$, which represent a phase transition at $T_c \equiv JN/2k_B$ between the ferromagnet and paramagnet states (Fig. 2). 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 quasiphase transition between the quasiferromagnet and quasiparamagnet states. Such a quasiphase transition is manifest even in finite systems with $N = 100 \sim 1000$.

The specific heat and the magnetization take nonzero values for $T > T_c$ [Fig. 2(a) and 2(c)], which is zero in the limit $N \to \infty$. 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 quasiparamagnet state. The maximum value of the susceptibility increases linearly as N becomes large. It is an indicator of the quasiphase transition.

We proceed to investigate how thermodynamical properties of the nanodisk are 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]

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

$$H_T = \tilde{t} \sum_{k\sigma} \sum_{\alpha} [c_{k\sigma}^\dagger d_\sigma(\alpha) + d_\sigma^\dagger(\alpha) c_{k\sigma}], \tag{3b}$$

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 $n_{\rm tot}$ 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.

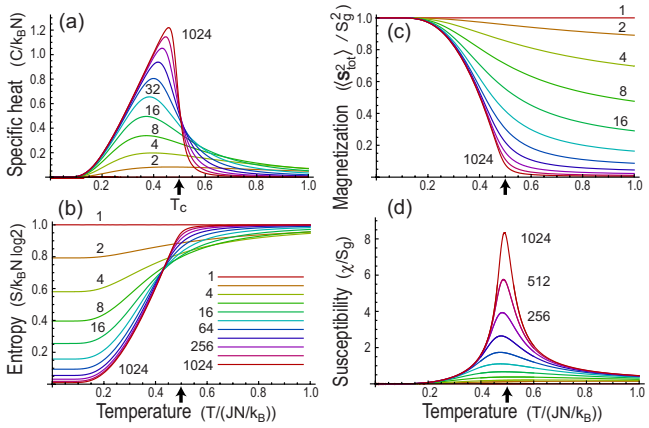

FIG. 2. (Color online) Thermodynamical properties of the nanodisk without leads. (a) The specific heat C in unit of k_BN. (b) The entropy S in unit of $k_B N$ log 2. (c) The magnetization $\langle \boldsymbol{S}_{\rm tot}^2 \rangle$ in unit of S_g^2. (d) The susceptibility χ in unit of S_g. Curves are in sequential order for the size $N = 1, 2, 2^2, \ldots, 2^{10}$, as indicated. The horizontal axis stands for the temperature T in unit of JN/k_B. The arrow represents the phase-transition point T_c in the limit $N \to \infty$.

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[11] to eliminate H_T, $H \to \tilde{H} = e^{iG} H e^{-iG}$, with G as the generator satisfying $H_T + \frac{i}{2}[G, H_0] = 0$. 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 $\tilde{H} = H_D + H_L + H_K + O(\tilde{t}^3)$, where H_K is the second-order term in $\tilde{t}$. It is the many-spin Kondo Hamiltonian,

$$H_K = J_K \sum_{kk'\sigma\sigma'} c_{k\sigma}^\dagger \boldsymbol{\tau}_{\sigma\sigma'} c_{k'\sigma'} \cdot \boldsymbol{S}_{\rm tot}, \tag{4}$$

with the Kondo coupling constant $J_K = 8\tilde{t}^2/U'$.

The total Hamiltonian is now given by $H_{\rm eff} = H_S + H_L + H_K$ at half filling. We define the spinor $\psi = (c_\uparrow, c_\downarrow)^t$. The partition function in the Matsubara form is given in terms of the Hamiltonian density $\mathcal{H}_{\rm eff}$ as

$$Z = {\rm Tr}_S \int \mathcal{D}\psi \mathcal{D}\psi^\dagger \exp\left[- \int_0^\beta d\tau \int dx (\psi^\dagger \partial_\tau \psi + \mathcal{H}_{\rm eff}) \right]$$
$$= {\rm Tr}_S [\exp(-\beta H_S) Z_K], \tag{5}$$

with $Z_K = \int \mathcal{D}\psi \mathcal{D}\psi^\dagger \exp[-S_K]$, where S_K is the action $S_K = \int_0^\beta d\tau \int dx (\psi^\dagger \partial_\tau \psi + \mathcal{H}_L + \mathcal{H}_K)$. 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 Eq. (5).

Because an electron in the lead is constrained within a very narrow region, it is a good approximation to neglect momentum scatterings,

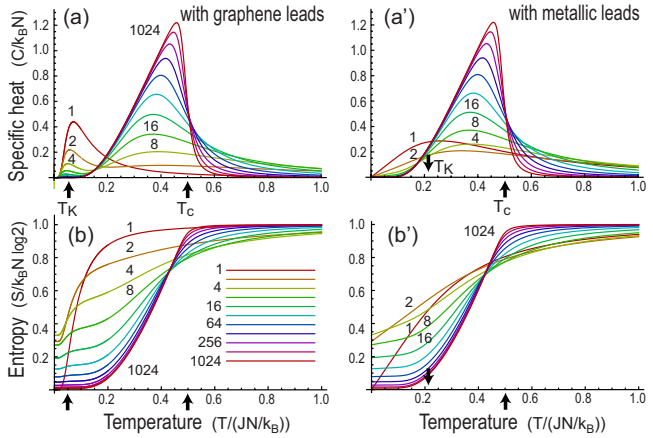

FIG. 3. (Color online) Thermodynamical properties of the nanodisk (a) and (b) with graphene leads and (a') and (b') with metallic leads. See the caption of Fig. 2. We have set $J_K/J=0.2$ and $D=2k_BT_c$. A new peak appears around T_K in the specific heat.

$$H_K \simeq 2J_K \boldsymbol{s}\cdot\boldsymbol{S}_{\rm tot}, \tag{6}$$

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

$$S_K=\int \frac{d\omega}{2\pi}\sum_k \psi^\dagger(k)M(k)\psi(k), \tag{7}$$

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

$$F_K=-\frac{1}{2\beta}\sum_k \ln\{\cosh(\beta J_K|\boldsymbol{S}_{\rm tot}|)+\cosh[\beta\varepsilon(k)]\}. \tag{8}$$

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

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 functional integration (8) is quite simple,

$$F_K=-\frac{1}{\beta}\ln\cosh[\beta J_K|S_{\rm tot}|/2]. \tag{9}$$

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 Eq. (5),

$$Z=\sum_S (2S+1)g_N(S)e^{-\beta JS(S+1)}\cosh\left(\frac{\beta J_K}{2}\sqrt{S(S+1)}\right). \tag{10}$$

We compare thermodynamical properties of the nanodisk with leads (Fig. 3) and without leads (Fig. 2). The magnetization $\langle \boldsymbol{S}_{\rm tot}^2\rangle$ and the susceptibility χ 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 $T=T_K$

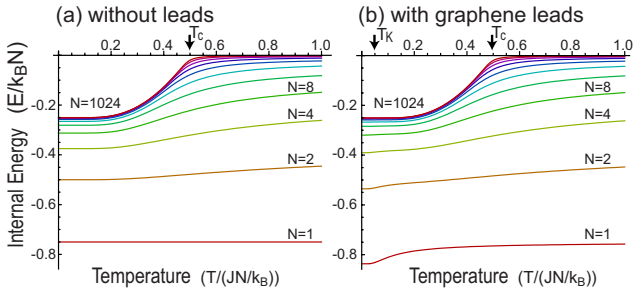

FIG. 4. (Color online) The internal energy E in unit of Nk_B for the nanodisk (a) without leads and (b) with graphene leads. See the caption of Fig. 2. (a) The energy decreases except for $N=1$ as the temperature decreases, which represents the ferromagnetic order. (b) There exists an additional energy decrease around T_K, which is prominent for $N=1$, attributed to the Kondo effect.

$\approx(J_K/2J)T_c$, 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 as

$$E_G(T)\simeq -JS_g^2-\frac{J_K}{2}S_g+J_KS_ge^{-\beta J_KS_g}. \tag{11}$$

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 $S_G(0)-S(0)=-k_B\log 2$ as it 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 $|\langle \boldsymbol{s}\cdot\boldsymbol{S}_{\rm tot}\rangle|$ is calculated based on partition function (5) and shown in Fig. 5(a). Near zero temperature we find

$$|\langle \boldsymbol{s}\cdot\boldsymbol{S}_{\rm tot}\rangle|\simeq\frac{1}{2}S_g\tanh[\beta J_KS_g/2]. \tag{12}$$

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 quasiparamagnet phase for large N since $\langle \boldsymbol{S}_{\rm tot}\rangle\approx 0$. We may interpret these phenomena as follows. Electrons in the lead and the nanodisk form spin-singlet states to lower the coupling energy [Eq. (6)]. The singlet state is rather tight for $T\lesssim T_K$ but thermally broken as T increases.

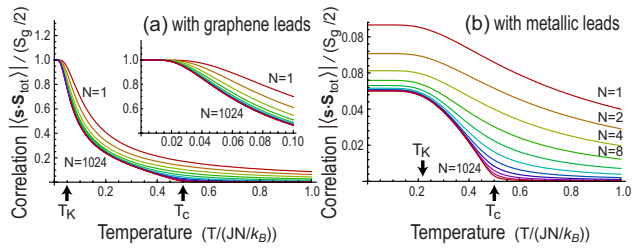

FIG. 5. (Color online) The spin-spin correlation $|\langle \boldsymbol{s}\cdot\boldsymbol{S}_{\rm tot}\rangle|$ in unit of $S_g/2$. See the caption of Fig. 3. The correlation occurs due to the Kondo coupling. It is almost constant for $T\lesssim T_K$, and decreases as T increases.

Next we consider the system comprised of metallic leads with a constant energy density, $\rho(\varepsilon)=\rho$ for $|\varepsilon|<D$ and $\rho(\varepsilon)=0$ for $|\varepsilon|>D$. We change the momentum integration into the energy integration in Eq. (8),

$$F_{\mathrm{K}} = -\frac{\rho}{2\beta}\int_{-D}^{D} d\varepsilon \, \ln[\cosh \beta J_{\mathrm{K}}|\boldsymbol{S}_{\mathrm{tot}}| + \cosh \beta\varepsilon]. \quad (13)$$

The free energy is given by $F_{\mathrm{K}}=-\rho\beta^{-2}[\beta^2 D J_{\mathrm{K}}|\boldsymbol{S}_{\mathrm{tot}}| - 2\beta D \log 2 + \mathrm{Li}_2(-e^{\beta(D-J_{\mathrm{K}}|\boldsymbol{S}_{\mathrm{tot}}|)}) - \mathrm{Li}_2(-e^{-\beta(D+J_{\mathrm{K}}|\boldsymbol{S}_{\mathrm{tot}}|)})]$, where $\mathrm{Li}_2[x]$ is the dilogarithm function.[12] It is reduced to the free energy of the nanodisk with graphene leads in the limit $D\to 0$ with $\rho=1/2D$.

The magnetization $\langle \boldsymbol{S}_{\mathrm{tot}}^2 \rangle$ and the susceptibility χ are found to be indistinguishable from those in the case of no leads (Fig. 2). The relation $S_{\mathrm{M}}(0)-S(0)=-k_{\mathrm{B}}\log 2$ holds for the entropy precisely as in the case of graphene leads. In Fig. 3, we show the specific heat $C_{\mathrm{M}}(T)$ and the entropy $S_{\mathrm{M}}(T)$ for various size N. A broad peak appears at $T=T_{\mathrm{K}}$ in the specific heat. Using the asymptotic behaviors[12] of $\mathrm{Li}_2[x]$, we obtain the free energy in low-temperature regime as

$$F_{\mathrm{K}} \simeq \frac{-\rho}{\beta}\left[\beta D J_{\mathrm{K}}|\boldsymbol{S}_{\mathrm{tot}}| - 2D\log 2 + \frac{\pi^2}{6\beta} + \frac{\beta}{2}(D - J_{\mathrm{K}}|\boldsymbol{S}_{\mathrm{tot}}|)^2\right], \quad (14)$$

which is valid up to the terms in the order of $e^{-\beta D}$. The entropy $S_{\mathrm{M}}(T)$, the specific heat $C_{\mathrm{M}}(T)$, and the internal energy $E_{\mathrm{M}}(T)$ read as follows:

$$S_{\mathrm{M}}(T) \simeq k_{\mathrm{B}} \log\frac{N+1}{2} + \frac{\pi^2}{3}\rho k_{\mathrm{B}}^2 T, \quad C_{\mathrm{M}}(T) \simeq \frac{\pi^2}{3}\rho k_{\mathrm{B}}^2 T, \quad (15)$$

and $E_{\mathrm{M}}(T)=E_{\mathrm{G}}(T)+\Delta E(T)$ with

$$\Delta E(T) \simeq -\frac{\rho}{2}(D - J_{\mathrm{K}}S_g)^2 + \frac{\pi^2}{6}\rho(k_{\mathrm{B}}T)^2. \quad (16)$$

All terms proportional to ρ have arisen from free electrons in the metallic lead. The internal energy $E_{\mathrm{M}}(T)$ consists of two terms: $E_{\mathrm{G}}(T)$ is identical to energy (11) 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 bandwidth of free electrons in the lead becomes narrower due to the Kondo coupling. We may interpret that n free electrons with

$$n = \rho J_{\mathrm{K}} S_g \quad (17)$$

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 $|\langle \boldsymbol{s}\cdot\boldsymbol{S}_{\mathrm{tot}}\rangle|$ in Fig. 5(b). The overall features are the same as for the nanodisk with graphene leads. However, there are other 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 Eq. (17). Indeed, it is observed that $|\langle \boldsymbol{s}\cdot\boldsymbol{S}_{\mathrm{tot}}\rangle| \to \frac{1}{2}\rho J_{\mathrm{K}} S_g$ at $T=0$ as $N\to\infty$ [Fig. 5(b)].

In this Rapid Communication 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.[10] We have shown various thermodynamical results indicating many-spin Kondo effects.

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