Gapless Spin-1 Neutral Collective Mode Branch for Graphite

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Using the standard tight binding model of 2D graphite with short range electron repulsion, we predict a gapless spin-1, neutral collective mode branch *below the particle-hole continuum* with energy vanishing linearly with momenta at the Γ and K points in the Brillouin zone. This spin-1 mode has a wide energy dispersion, 0 to $\sim$2 eV, and is not Landau damped. The "Dirac cone spectrum" of electrons at the chemical potential of graphite generates our collective mode, so we call this "spin-1 zero sound" of the "Dirac sea." Epithermal neutron scattering experiments and spin polarized electron energy loss spectroscopy can be used to confirm and study our collective mode.

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Graphite is an important system in condensed matter science and technology; in carbon research its role is fundamental. Its electrical and magnetic properties have been investigated for decades both experimentally and theoretically [1]. It is one of the simplest of quasi-two-dimensional zero gap semiconductors/semimetals. Intercalated graphites offer many phases of condensed matter including superconductivity. Other important systems such as Bucky balls, carbon nanotubes [2], and some form of amorphous carbon derive many of their novel properties from their underlying "graphite character." Any newer understanding of graphite is likely to have a wider impact.

The aim of this Letter is to predict a simple but important property of graphite that calls for reexamination of some of the low energy electrical and magnetic properties of graphite. We find that graphite possesses a new, unsuspected gapless branch of a spin-1 and charge neutral collective mode. This branch lies below the electron-hole continuum (Fig. 2 below); its energy vanishes linearly with momenta as $\hbar\omega_s \approx \hbar v_F q(1 - \alpha q^2)$ about three points (Γ, K, K') in the Brillouin zone (BZ) (Fig. 1).

The simplicity of our model makes the result quite interesting. Our spin-1 mode survives in carbon nanotubes and has fascinating consequences [3]. Consequently graphite and nanotubes are capable of supporting a stable and coherent "neutral spin current" of our excitation at low energies, unknown in nonmagnetic solids. Some new ideas on (i) spin-based electronics and (ii) a qubit for quantum computation that utilizes our novel spin current in graphite and nanotubes will be discussed elsewhere [3].

Since graphite interpolates metals and insulators, our collective mode can be viewed from both the metallic and the insulating standpoint. In paramagnetic metals "zero sound" is a Fermi surface collective mode [4]. The "charge" as well as the "spin" of a Fermi sea can undergo independent oscillations. The charge oscillation becomes a high energy branch, the plasmon, because of the long range Coulomb interaction; plasmons in graphite have been studied in great detail in the past [5]. The electron-electron interactions in normal metals do not usually manage to develop a low energy spin collective mode branch because of the nature of the particle-hole spectrum. However, *the particle-hole spectrum of 2D graphite with a "window" (Fig. 2) provides a unique opportunity for a spin-1 collective mode branch to emerge in the entire BZ.* From this point of view our spin-1 collective mode is a "spin-1 zero sound" of a (2 + 1)-dimensional "massless Dirac sea," rather than a "Fermi sea."

From an insulator point of view our collective mode is a spin-triplet exciton branch. Triplet excitons are well known in insulators, semiconductors, and $p\pi$ bonded planar organic molecules; however, they usually have a finite energy gap, except when there are magnetic instabilities.

Our spin-1 collective mode may be thought of as a manifestation of Pauling's [6] resonating-valence—bond (RVB) state of graphite: the spin-1 quanta is a delocalized triplet bond in a sea of resonating singlets. The gaplessness makes it a "long range RVB" rather than Pauling's short range RVB. Later we will present an argument to

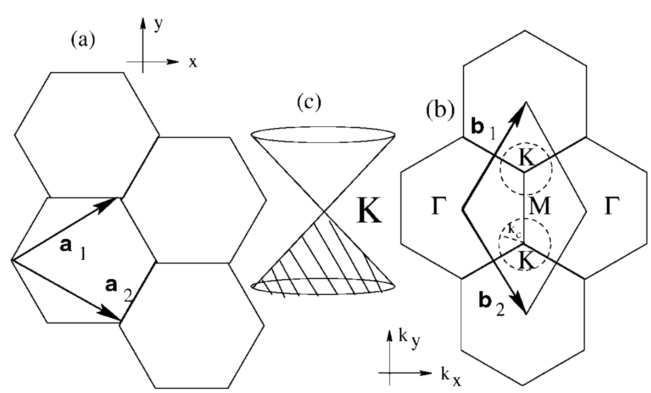

FIG. 1. (a) Honeycomb lattice, $\mathbf{a}_{1,2} = \frac{a}{2}(\sqrt{3}, \pm 1)$. (b) The Brillouin zone, $\mathbf{b}_{1,2} = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, \pm 1)$. (c) Dirac cone spectrum at a K point.

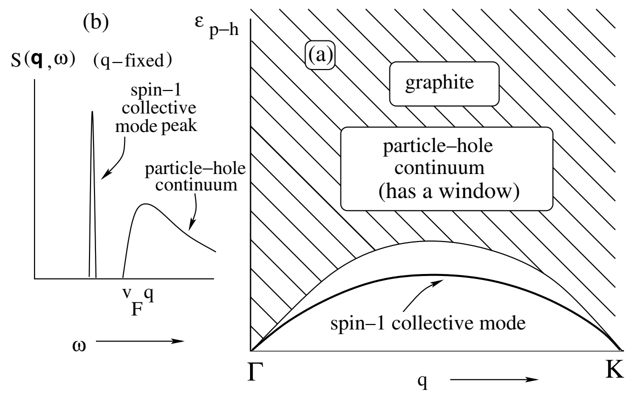

FIG. 2. (a) Particle-hole continuum with a window for graphite. (b) $S(\mathbf{q}, \omega)$ for $q > q_c(\sim \frac{1}{50}\frac{\pi}{a})$.

suggest that at low energies the neutral spin-1 excitation might undergo quantum number fractionization into two spin-$\frac{1}{2}$ spinons.

The existence of our gapless spin-1 collective mode branch should influence the spin part of the magnetic susceptibility, rather than the orbital part, which for graphite is diamagnetic, large, and anisotropic. Study of spin susceptibility by ESR, NMR, and inelastic neutron scattering are good probes to detect the low energy part of our collective modes over a limited energy up to ~50 meV. Our spin-1 collective mode introduces a magnetic instability in the presence of magnetic field, which will be discussed in a future publication. This may explain a recent observation of ferromagnetism in oriented pyrolitic graphite by Kopelevich and collaborators [7]. Our mode could be probed over a large energy range, by epithermal neutrons and spin polarized electron energy loss spectroscopy (SPEELS) [8]. In view of a wide energy scale associated with the collective modes, probes such as two magnon Raman scattering, angle-resolved photoemission spectroscopy, scanning tunneling microscopy, and spin valves [9] should also be tried.

The importance of electron-electron interaction in graphite [10,11] and nanotubes [12,13] has been realized recently and it has led to several interesting studies and predictions. 2D cuprates with the Dirac cone spectrum have been studied in the context of antiferromagnetic (AFM) order in the Mott insulating RVB-flux phase, for spin-1 goldstone modes [14], and d-wave superconducting phases, for spin-1 collective modes [15].

Real graphite is a layered semimetal—stacked layers of a honeycomb lattice of carbon atoms. We have one p_z orbital as the relevant valence orbital and one electron per carbon atom. The $p\pi$ bond produces a filled valence band and an empty conduction band with vanishing band gaps at two K points in the BZ. The coupling between graphite layers is van der Waals–like. However, a small "coherent" interlayer hopping has been invoked to explain the presence of small electron and hole tubes and pockets (with 10^{-4} carriers per carbon atom, i.e., a Fermi energy $\epsilon_F \sim 100$–200 K), responsible for the semimetallic character of graphite.

We start with a two-dimensional Hubbard model for graphite, which captures the physics of low energy spin dynamics. The Hamiltonian is

$$H = -t \sum_{\langle i,j\rangle,\sigma} (c^\dagger_{i,\sigma} c_{j,\sigma} + \text{H.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow}.$$

Here $t \sim 2.5$ eV is the nearest-neighbor hopping matrix element. While the bare atomic U is of the order of 8 eV, the effective renormalized U can be of the order of 3–4 eV. We will keep U as a parameter to be fixed by experiment.

The dispersion relation for the $p\pi$ bands is

$$\varepsilon_{\mathbf{k}} = \pm t \sqrt{1 + 4\cos\frac{\sqrt{3}\,k_x a}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}} \qquad (1)$$

with vanishing gaps at the two K points in the BZ (Fig. 1). The particle-hole continuum of excitations is shown in Fig. 2. The "Dirac cone single-particle spectrum" at the Γ and K points makes the particle-hole continuum very different from that of a free Fermi gas, or systems with extended Fermi surface. In contrast to Fig. 3, the particle-hole spectrum of a 2D Fermi liquid, our spectrum has a window. *The window is characteristic of a 1D particle-hole spectrum.* In the Hubbard model two particles with opposite spins at a given site repel with an energy U. This means an attraction for an up-spin particle and down-spin hole, or an attraction in the spin-triplet channel for a particle-hole pair. A spin-triplet particle-hole pair could form a bound state, provided there is sufficient phase space for the attractive scattering. We find one spin-1 bound state for every center of mass momentum of the particle-hole pair. In particular an effective 1D character of phase space also makes the collective mode energy vanish linearly with momenta around the three points: Γ and K's.

The collective mode that we are after is obtained as the poles of the particle-hole response function in the spin-triplet channel. We will focus on the zero temperature case. The magnetic response function within the RPA (particle-hole ladder summation) is given by

$$\chi(\mathbf{q}, \omega) = \frac{\chi^0(\mathbf{q}, \omega)}{1 - v(\mathbf{q})\chi^0(\mathbf{q}, \omega)}. \qquad (2)$$

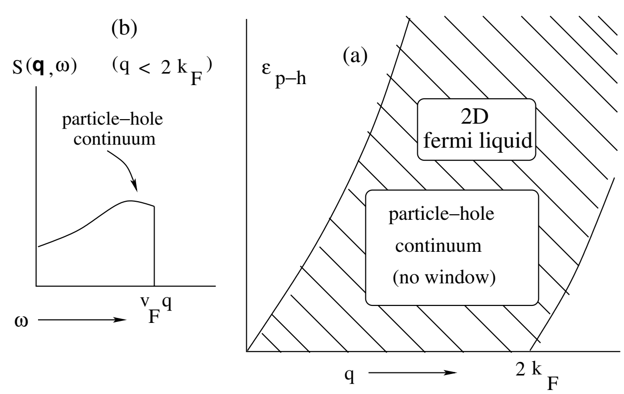

FIG. 3. (a) Particle-hole continuum without a window for a 2D Fermi gas. (b) $S(\mathbf{q}, \omega)$ for $q < 2k_F$.

For the Hubbard-type on-site repulsion, $v(\mathbf{q}) = U$ and the *free particle* susceptibility is

$$\chi^0(\mathbf{q}, \omega) = \frac{1}{N} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}+\mathbf{q}} - f_{\mathbf{k}}}{\hbar\omega - (\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}})}. \quad (3)$$

Here f's are the Fermi distribution functions. We have evaluated the RPA response function numerically and found the collective mode branch in the entire BZ, below the particle-hole continuum. However, it is instructive to linearize the electron and hole dispersion for low energies, a Dirac cone approximation [10], and to get an analytical handle. We linearize the dispersion around K and K' and replace the BZ by two circles of radii k_c (Fig. 1):

$$\varepsilon_{\mathbf{k}} = \pm\hbar v_F|\mathbf{k}| \quad \text{for } k < k_c, \quad (4)$$

where $v_F = \frac{\sqrt{3}}{2}\frac{a}{\hbar}t$ and N is the number of unit cells. In our linearization scheme, in Eq. (4) the summation is over the two circular patches (Fig. 1b).

For q, ω small and below the particle-hole continuum, $\mathrm{Im}\chi^0(\omega, \mathbf{q})$, we obtain an exact asymptotic form [10]:

$$\mathrm{Im}\chi^0(\mathbf{q}, \omega) = \frac{a^2q^2}{16\hbar\sqrt{\omega^2 - (qv_F)^2}} \sim \frac{a^2q^{3/2}}{16\hbar\sqrt{2v_F}\sqrt{\omega - qv_F}},$$

with a square root divergence at the edge of the particle-hole continuum in $(\omega, \mathbf{q})$ space. This expression has the same form as the density of states (DOS) of a particle in 1D (with energy measured from $\hbar v_F q$). Note that, in fact, $\mathrm{Im}\chi^0(q, \omega) = \pi\rho_q(\omega)$, where $\rho_q(\omega)$ is the free particle-hole pair *DOS* for a fixed center-of-mass momentum q. *That is, the particle-hole pair has a phase space for scattering which is effectively one dimensional.* Thus we have a particle-hole bound state in the spin-triplet channel for arbitrarily small U. However, we also have a prefactor $q^{3/2}$ that scales the density of states. This together with the square root divergence of the density of states at the bottom of the particle-hole continuum gives us a bound state for every $\mathbf{q}$ as $q \to 0$, with the binding energy vanishing as αq^3, as shown below. The square root divergence has the following phase space interpretation. The constant energy ($\hbar\omega$) contour of a particle-hole pair of a given total momentum q defines an ellipse in k space: $\omega = v_F(|\mathbf{k} + \mathbf{q}| + |\mathbf{k}|)$. As the energy of the particle-hole pair approaches the bottom of the continuum, i.e., $\epsilon_{p-h} \to \hbar v_F q$, the minor axes of the ellipses become smaller and smaller and the elliptic contours degenerate into parallel line segments of effective length $\sim q^{3/2}$. The asymptotic equispacing of these line segments leads to an effective one dimensionality and the resulting square root divergence.

According to (1), the collective mode in the *magnetic* channel is the solution of

$$1 - U\chi^0(\mathbf{q}, \omega) = 0$$

or, equivalently, $\mathrm{Im}\chi^0(\mathbf{q}, \omega) = 0$ and $\mathrm{Re}\chi^0(\mathbf{q}, \omega) = \frac{1}{U}$. The asymptotic expression for $\mathrm{Re}\chi^0(\mathbf{q}, \omega)$ is found to be

$$\mathrm{Re}\chi^0(\mathbf{q}, \omega) \approx \frac{a^2}{4\pi v_F\hbar} \times \left[k_c + \frac{q\sqrt{2}}{\sqrt{1 - z}} \arctan\left(\frac{\sqrt{2}}{\sqrt{1 - z}}\right)\right],$$

where $z \equiv \frac{\omega}{qv_F}$. By using the above expression, we obtain the following dispersion relation for the collective mode:

$$\omega = qv_F - \frac{q^3a^4}{32v_F(\frac{\hbar}{U} - \frac{k_ca^2}{4\pi v_F})^2} \equiv qv_F - E_B(q) \quad (5)$$

as $\omega \to q \to 0$. Here $E_B(q)$ is the *binding* energy of the particle-hole pair of momentum q around the Γ point. The binding energy around the K points is roughly twice this.

We mentioned earlier that our collective mode is a "magnetic zero sound." While magnetic zero sound is difficult to obtain in normal metals, graphite manages to obtain it in the entire BZ because of the window in the particle-hole spectrum (Fig. 2).

Having established the existence of a gapless spin-1 collective mode branch within the Hubbard model and the RPA approximation, we will discuss whether the semimetallic screened interaction of 3D stacked layers will affect our result. As mentioned earlier, in tight binding situation like ours, the spin physics is mostly captured by the short range part of the repulsion among the electrons. We have numerically studied the response function for a more realistic intralayer interaction, namely, the screened Coulomb interaction (including interlayer scattering between layers separated by distance d) given by [10]

$$\tilde{v}(\omega, q) = \frac{2\pi e^2}{\epsilon_0 q} \frac{\sinh(qd)}{\sqrt{[\cosh(qd) + \frac{2\pi e^2}{\epsilon_0 q}\sinh(qd)\chi_0(\omega, q)]^2 - 1}}$$

and find that the collective mode survives with small quantitative modifications.

Let us discuss lifetime effects, that are beyond RPA. A remarkable feature of our collective mode is that it never enters the particle-hole continuum. It does not suffer from Landau damping (resonant decay into particle-hole pair excitations). To this extent our collective modes are sharp and protected; higher order processes will produce the usual lifetime broadening, particularly at the high energy end. However, in real graphite there are tiny electron and hole pockets in the BZ with a very small Fermi energy $\sim$10 to 20 meV. This leads to "Landau damping" of low energy collective modes around the Γ and K points, but only in a small momentum region $\Delta k \sim 2k_F \sim \frac{1}{50}\frac{\pi}{a}$, where k_F is the mean Fermi momentum of the electron and hole pockets. That is, only a few percent of the collective mode branch in the entire BZ is Landau damped.

A small interlayer hopping between neighboring layers $t_\perp \sim 0.2$ eV ($\ll$2.5 eV, the in-plane hopping matrix element) has always been invoked in the band theory approaches to understand various magneto-oscillation experiments and also c-axis transport in graphite. However, a strong renormalization of $t_\perp$ is possible, as an anomalously large anisotropic resistivity ratio $\frac{\rho_c}{\rho_{ab}} \sim 10^4$ has been reported in some early experiments on graphite single crystals; a many-body renormalization is also partly implied by the existence of our spin-1 collective mode at low energies. Since the emergence of the small electron and hole pockets (cylinders) are due to interlayer hopping, interlayer hopping affects the spin-1 collective modes only in a small window of energy 0 and ~0.1 eV. For the same reason the collective modes do not have much dispersion along the c axis.

Within our RPA analysis the collective mode frequency becomes negative at the Γ point for $U > U_c \sim 2t$. Because there are two atoms per unit cell, this could be either an antiferromagnetic or ferromagnetic instability. Other studies [11,16] have indicated an AFM instability for $U > U_c \sim 2t$.

Now we discuss the experimental observability of the spin-1 collective mode branch. The collective mode has a wide energy dispersion from 0 to ~2 eV. The low energy 0 to 0.05 eV part of the collective modes determines the nature of the spin susceptibility [Eq. (3)] of graphite and leaves its signatures in NMR and ESR results. For higher energies we have to use other probes.

Inelastic neutron scattering can be used to study the line shapes and dispersion of our spin-1 collective modes. However, epithermal neutrons in the energy range 0.1 to ~1 eV, rather than the cold and thermal, 0.2 to 50 meV, neutrons are needed in our case, due to the large energy dispersion. The dynamic structure factor $S(\mathbf{q}, \omega)$ as measured by inelastic neutron scattering is obtained by using our calculated RPA expression for our magnetic response function using the relation

$$(1 - e^{-\beta\omega})S(\mathbf{q}, \omega) = -\frac{1}{\pi}\,\mathrm{Im}\chi(\mathbf{q}, \omega). \qquad (6)$$

At the present moment, one need not concentrate on the energy resolution, and it would be good to focus on proving the existence of the spin-1 collective mode by neutron scattering experiments. As the single-phonon density of states of graphite vanish for energies >0.2 eV, one need not perform spin polarized neutron scattering in order to avoid single-phonon peaks.

Another probe for studying the spin-1 collective mode is SPEELS; exchange interaction of the probing electron with the π electrons of graphite can excite the spin-1 collective mode. Since the electron current and spin depolarization essentially measure the magnetic response function, our calculation of $\chi(\mathbf{q}, \omega)$ [Eq. (2)] can be profitably used to interpret the experimental results.

The square root divergence of the density of states at the bottom edge of the particle-hole continuum tells us that *the low energy spin physics is effectively one dimensional*. To that extent, *in a final theory,* we may expect our spin-1 excitation to be a triplet bound state of "two neutral spin-$\frac{1}{2}$ spinons" rather than "e^+e^- electron-hole pairs." Further, as the energy of the spin-1 quantum approaches zero the binding energy also approaches zero and the electron-hole bound state wave function becomes elliptical, with diverging size. We may then view the low energy spin-1 quanta as a "critically (loosely) bound" two spinon state, very much like the quantum number fractionization of the des Cloizeaux-Pearson spin-1 excitation in the 1D spin-$\frac{1}{2}$ antiferromagnetic Heisenberg model. Our result also suggests a nonlinear sigma model and novel $(2 + 1)$-dimensional bosonization scheme for graphite [17].

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