Phase of magneto-oscillations in graphite

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The problem of Dirac fermions in graphite subject to a perpendicular magnetic field is studied. We show analytically that the weak-interlayer interaction between the graphene sheets leads to anomalies in the Shubnikov-de Haas and de Haas-van Alphen magneto-oscillations governed by the orbits around extremal cross sections of the graphite Fermi surface. The calculation of the Landau plot performed within a four-band continuum model reveals that magneto-oscillations are aperiodic, except of the case of vanishing interlayer interaction at the H point of the graphite Brillouin zone. Also for all other orbits along the H-K-H edge the magneto-oscillations are only asymptotically periodic in the quasiclassical limit with the phase corresponding to massive fermions.

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Graphite is a layered material composed of weakly coupled two-dimensional (2D) graphene sheets formed by hexagonally arranged carbon atoms. In 2004, a single sheet of graphene was prepared from three-dimensional (3D) graphite by micromechanical cleavage.[1] The discovery immediately attracted attention of the solid-state physical community, as the electrons in graphene obey a linear energy dependence on the wave vector k, and behave like massless relativistic particles—Dirac fermions (DFs). In a magnetic field B, the Landau-level (LL) energies of DFs are proportional to $\sqrt{B}$ instead of the linear dependence on B typical for massive Schrödinger fermions (SFs). In the seminal papers,[1–3] the Shubnikov-de Haas (SdH) magneto-oscillations (MOs) in graphene were found periodic in $1/B$, similarly as in the case of a 2D gas of massive SFs, but with the phase shifted by π. The shift, which was clearly demonstrated by the Landau plot of magnetoresistance oscillations, is due to the existence of the zero-energy LL, shared by electrons and holes. For the same reason, the anomalous quantum-Hall effect with a half integer instead of integer quantization was observed in mechanically exfoliated samples.[2] This is considered as the most direct evidence of DFs in graphene. In 2006, important technological progress was achieved. The epitaxial graphene was grown on the single-crystal silicon carbide by vacuum graphitization.[4,5]

The discovery of DFs in graphene has resulted in renewed interest in bulk graphite. The possible coexistence of both carrier types was expected in this material. The low-energy linear dispersion near the H point of the graphite Brillouin zone was found by the angle-resolved photoemission spectroscopy.[6] The magnetotransmission[7] and scanning tunneling spectroscopy experiments[8] showed LL spectra characteristic of both DFs and SFs. In a series of papers,[9–11] the spectral analysis of SdH and de Haas-van Alphen (dHvA) oscillations was employed to determine the phases of two series of MOs observed in graphite. Based on their analysis, the authors of Refs. 9–11 came to a conclusion that one of two groups of oscillating carriers corresponds to DFs. Recently, a paper[12] was devoted to a careful, mostly experimental investigation of SdH effect in graphite, where doubts about the observation of DFs using magnetotransport measurements were expressed.

Here the problem is treated from the theoretical point of view. We construct a Landau plot for the model Hamiltonian developed by Slonczewski, Weiss, and McClure (SWM) (Refs. 13–15) and compare the result with Landau plots for SFs and DFs, which are described below.

The energy spectra of 2D SFs and DFs in a zero magnetic field can be written as

$$E^S(k) = \frac{\hbar^2 k^2}{2m^*}, \quad E^D(k) = \pm \hbar v_F k, \tag{1}$$

where $k=\sqrt{k_x^2+k_y^2}$, m^* is the effective mass of SFs, and v_F is the Fermi velocity of DFs. The positive and negative branches of the conical DFs spectrum correspond to the electrons and holes, respectively.

In a magnetic field, the spectra of SFs and DFs are quantized into the LLs as follows:

$$E_n^S = \hbar\omega_c\left(n+\frac{1}{2}\right), \quad E_n^D = \pm\sqrt{2\hbar|e|v_F^2 Bn}, \tag{2}$$

where $\omega_c=|e|B/m^*$ is the cyclotron frequency and the index $n=0,1,2,\ldots$. In the case of SFs the equidistant LLs lie above $E=0$ for any finite B, whereas in the DFs case the lowest-electron LL is shared with the highest-hole LL located exactly at $E=0$.

The Eq. (2) is consistent with the Onsager-Lifshitz quasiclassical quantization rule

$$A^Q(E_F) = \frac{2\pi|e|B}{\hbar}(n+\gamma^Q), \quad Q=S,D, \tag{3}$$

where $A^Q(E_F)=\pi k_F^2$ is the area of the SF or DF Fermi circle, calculated with the Fermi energy E_F and the Fermi wave vector k_F taken from Eq. (1). We get $\gamma^S=1/2$ for SFs and $\gamma^D=0$ for DFs.

MOs observed in SdH and dHvA effects are controlled by oscillations of the density of states (DOS). It is well known that the DOS on the Fermi level, $g(E_F)$, can be expressed as an imaginary part of the resolvent $G(z)=(z-H)^{-1}$,

$$g(E_F) = -\frac{1}{\pi}\mathcal{I}m\ \mathrm{Tr}\ G(E_F + i0). \tag{4}$$

For simple diagonal Hamiltonians of SFs and DFs given by Eq. (2), we get

$$g^Q(E_F) = \frac{|e|B}{2\pi\hbar}\sum_{n=0}^{\infty}\delta(E_F - E_n^Q). \tag{5}$$

It follows from Eq. (5) that the DOS reaches maxima at magnetic fields B_n for which the LLs cross the Fermi energy E_F. A Landau plot, i.e., the plot of the inverse magnetic fields $1/B_n$ versus the level index n is a standard tool used to determine the frequency and phase of MOs. For SFs and DFs we arrive to

$$\frac{B_0^Q}{B_n} = n + \gamma^Q, \tag{6}$$

where $B_0^S = m^* E_F/(\hbar|e|)$ and $B_0^D = E_F^2/(2\hbar|e|v_F^2)$ are the oscillation frequencies, in agreement with the quasiclassical expression obtained from Eq. (3),

$$B_0^Q = \hbar A^Q/2\pi|e|. \tag{7}$$

It is clear that the positions of maxima of SF and DF oscillations differ by a half of the period, i.e., by π in terms of a phase factor.

In graphite, the interlayer interaction of Bernal-stacked graphenes adds a k_z dependence to the electron energy spectrum and a 3D Fermi surface (FS) is formed close to the H-K-H edge of the hexagonal Brillouin zone (BZ). As mentioned above, the graphite 3D electronic structure is described by the semiempirical SWM Hamiltonian, which employs seven nearest-neighbor tight-binding (TB) parameters $\gamma_0, \gamma_1, \ldots \gamma_5, \Delta$, and the value of the Fermi energy, E_F. Previously, the model parameters were fitted to various optical and transport experiments.[16] Recently, their values are continuously refined by fitting to the experimental data[12] and/or to the results of first-principles numerical simulations of the graphite band structure.[17]

Among the seven SWM parameters, the parameter γ_3, which controls the trigonal warping of the FS, brings a numerical complications in the case of nonzero magnetic field. When γ_3 is taken into account, the magnetic-field-SWM Hamiltonian has an infinite order and must be diagonalized numerically.[18] Fortunately, its influence is not too strong for k_z far from the K point of the BZ and energies close to E_F.[18] To facilitate our analytical treatment, we prefer to use a simplified Hamiltonian H with γ_3 neglected, in the form introduced in the McClure's paper.[15]

The choice of $\gamma_3 = 0$ yields isotropic equienergetic contours. The FS of graphite consists of elongated electron and hole pockets located near the points K and H with k_z-dependent circular cross sections. In the quasiclassical limit, two extremal cross sections define two series of MOs and two quasiclassical frequencies B_0^e and B_0^h for electrons and holes, respectively. Analytical solutions for the FS cross sections can be found, e.g., in Ref. 16.

With these approximations an expression similar to Eq. (6) can be obtained for any k_z-dependent cross section of the 3D graphite FS. To do so, we need to find the poles of the resolvent $G(z) = (E_F - H + i0)^{-1}$. In other words, we should solve the secular equation derived from the simplified Hamiltonian H of Ref. 15 for B_n, i.e., to find the roots B_n of the secular polynomial.

The solution yields a formula for the inverse magnetic fields as a function of the level index, n, in a shape

$$\frac{B_\pm^G(k_z)}{B_n} = \frac{n + \frac{1}{2} \pm \sqrt{\frac{1}{4} + n(n+1)\delta(k_z)}}{1 \pm \sqrt{\delta(k_z)}}, \tag{8}$$

where the three coefficients $B_\pm^G(k_z)$ and $\delta(k_z)$ can be derived from the SWM model and the value of E_F. The k_z dependence originates from $\cos(k_z c/2)$ which appears in the interlayer TB SWM parameters, $c/2$ denotes the interlayer distance in graphite. Obviously, $B_\pm^G(k_z)/B_n$, as given by Eq. (8), are not periodic in $1/B$.

An expression for the Landau plot corresponding to Eq. (8) can be written in a form

$$\frac{B_\pm^G(k_z)}{B_n} = n + \gamma_{\pm,n}^G(k_z). \tag{9}$$

In this equation $\gamma_{\pm,n}^G(k_z)$, defined by the right-hand side of Eq. (8), is not a constant describing the oscillation phase, but a variable which depends on the LL index n.

The dependence on n is most pronounced for high magnetic fields, i.e., for small n. In the low-magnetic-field limit, with a large number of LLs below E_F, we can write $n(n+1)\delta(k_z) \gg 1/4$ and $\sqrt{n(n+1)} \to n + 1/2$. Then $\gamma_{\pm,n}^G(k_z) \to 1/2$, and we can conclude that the charge carriers in graphite behave, at least as far as the phase is concerned, as the SFs.

Only when we can completely neglect the interlayer interaction, as at the H point of the 3D BZ, $k_z = \pi/c$, $\cos(k_z c/2) = 0$, $\Delta = 0$, and $\delta(k_z) \to 0$, we get

$$\frac{B_\pm^G(\pi/c)}{B_n} = n + \frac{1}{2} \pm \frac{1}{2}, \tag{10}$$

a result which corresponds to DFs.

In this paper, the Landau plots of two series of MOs, which can be observed in graphite, are considered as most interesting. We constructed them based on the parameters of the SWM model taken from Ref. 16. The explicit expressions for $B_\pm^G$ and $\delta(k_z)$, which appear in Eq. (8), will not be presented here. Instead, their k_z dependences are shown in Fig. 1 together with the contours of the FS. The positive sign applies in the formula (8) for k_z from the electron region of FS and the parameter B_+^G is equal to the quasiclassical frequency B_0^e. Similarly, the negative sign should be taken for k_z from the hole pockets, where B_-^G becomes equal to B_0^h. For both electron and hole extremal orbits the parameter δ is large and, consequently, the right-hand side of Eq. (8) can be approximated by $\sqrt{n(n+1)}$. The marked difference is only for $n = 0$. The Fig. 2 shows to what extent the accuracy of this approximation is reasonable.

The expression for $B_\pm^G/B_n$ is not periodic and the question arises how many LLs must be resolved to reach the linear

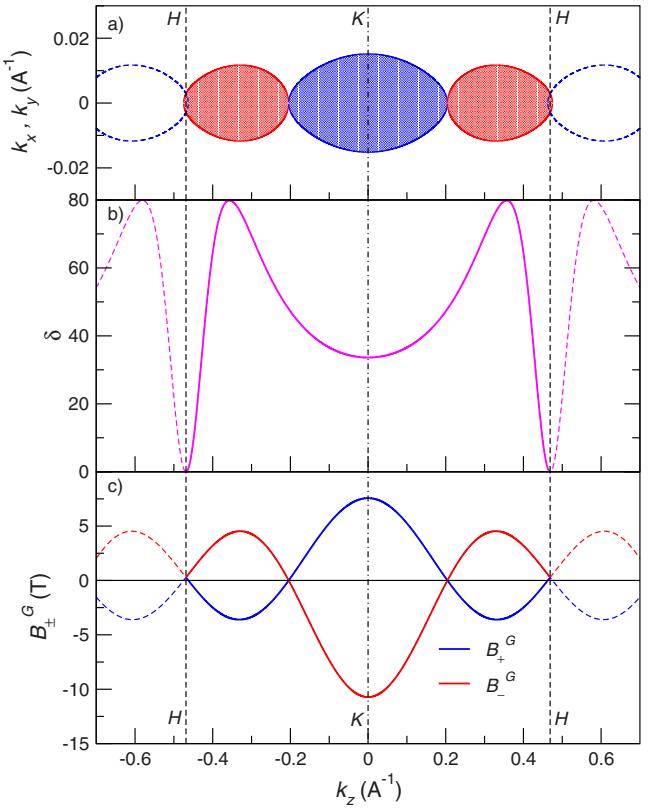

FIG. 1. (Color online) (a) Contours of the graphite Fermi surface, (b) a dimensionless parameter δ as a function of k_z, and (c) the parameters $B_\pm^G$ as functions of k_z.

dependence on n, i.e., the quasiclassical limit $n+1/2$. The result of the linear approximation of a model curve $\sqrt{n(n+1)}$ is presented in the inset of Fig. 2, where the relative deviations from the quasiclassical frequency and phase are shown. It turns out that both frequency and phase are underestimated if we took into account only limited number of n, $1 \leq n \leq N$. Less oscillations are necessary to get close to the quasiclassical frequency than to obtain a reasonable approximation for the phase. This may explain the differences found between the experimentally determined phases of samples with different mobilities, which are determined from different number of oscillations resolved.

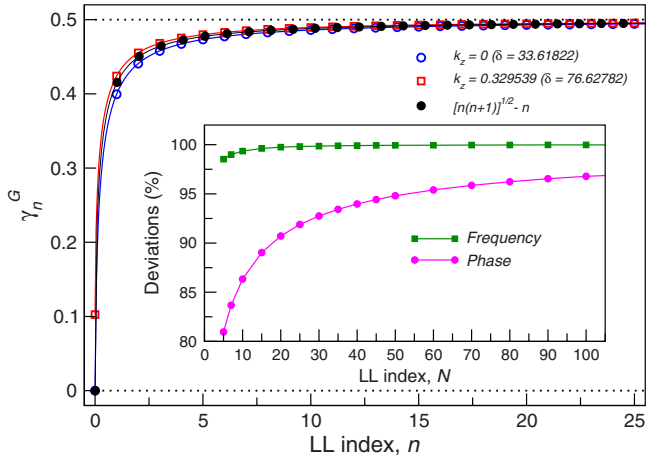

FIG. 2. (Color online) $\gamma_{\pm,n}^G(k_z)$ for maximum cross sections of the electron and hole pockets approximated by $\sqrt{n(n+1)}-n$. The inset shows results of the linear approximation of first N terms ($n=1,2,\ldots,N$) of $\sqrt{n(n+1)}$. The relative deviations from the quasiclassical frequency and phase are shown.

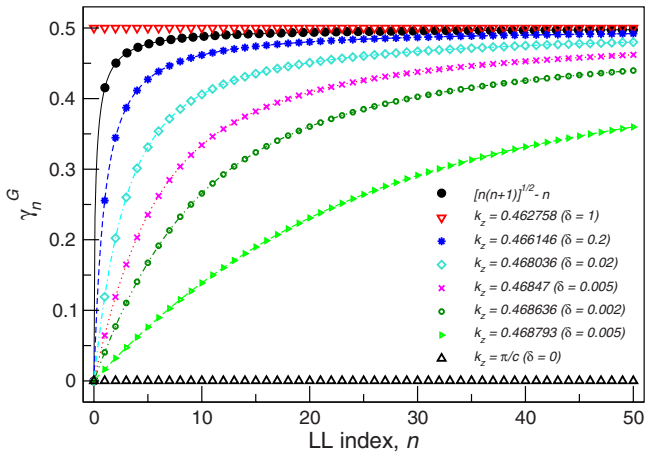

FIG. 3. (Color online) The dependence of $\gamma_{-,n}(k_z)$ on the LL index n for k_z close to the H point of the BZ.

Note that the above Landau plot can be derived if we approximate the energy spectra of electrons and holes by the formulas

$$E_n^e = \hbar\omega_c^e\sqrt{n(n+1)}, \quad E_n^h = \hbar\omega_c^h\sqrt{n(n+1)}, \tag{11}$$

where ω_c^e and ω_c^h are the quasiclassical cyclotron frequencies corresponding to extremal electron and hole orbits.

Two series of MOs discussed above correspond to $\delta \gg 1$ and to the maximum cross sections of the electron and hole pockets. There are another two extremal cross sections, till now not reliably resolved in the transport experiments, located around the H point of the BZ, where $\delta \leq 1$. In spite of the fact that, according to Ref. 18, the parameter γ_3 has a qualitative influence on the LLs structure near this point, it is at least of the theoretical interest to study the behavior of the $\gamma_{\pm,n}^G(k_z)$ for model with γ_3 neglected.

For a given k_z the dependence of the energy bands on k is hyperbolic in a zero magnetic field. While near the maximum cross sections there are broad minima/maxima of bands which are similar to parabolas for small k near the H point the hyperbolas are very sharp and with a shape close to the Dirac cone. Therefore, a smooth transition from SFs to DFs is expected. Figure 3 reveals that the behavior of $\gamma_{\pm,n}^G(k_z)$ is more complicated.

In the SWM model the k dependence of the zero-field energy at the H point (k_z=0) is given by

$$E^G = \frac{\Delta}{2} \pm \sqrt{\left(\frac{\Delta}{2}\right)^2 + \hbar^2 v_F^2 k^2}, \tag{12}$$

which is not equal to the Dirac cone for a finite Δ. Nevertheless, δ=0 implies that $\gamma_{-,n}^G(k_z)$ is a constant equal to 0, as for the DFs. This is in agreement with the Landau plot constructed from the energy spectra in a magnetic field, which according to Ref. 15 have a simple analytic form

$$E_n^G = \frac{\Delta}{2} \pm \sqrt{\left(\frac{\Delta}{2}\right)^2 + 2\hbar|e|v_F^2 Bn}. \quad (13)$$

On the other hand, the parameter δ equals 1 for E_F crossing the E_2 band of the SWM model. According to Eq. (8) this leads to $\gamma_{-,n}^G(k_z)=1/2$, as for the SFs, in spite of the k dependence not so close to parabolic one as the for the maximum cross sections, $\delta \gg 1$, where the energy spectra can be approximated by Eq. (11).

The field dependence of the corresponding LLs ranges from that described by Eq. (13) at the H point, which is close to $\sqrt{B}$ characteristic for DFs, to the linear dependence on B typical for SFs for extremal electron and hole orbits, as given by Eq. (11). It follows from the above discussion that the hyperbolic k dependence of the zero-field electron energy bands, which changes considerably depending on the value of k_z, yields aperiodic MOs when a magnetic field is applied. An exception is two k_z in the neighborhood of the H point of the BZ. We assume that this conclusion is at least qualitatively correct, as one can hardly believe that this is just the neglected γ_3 which yields the MO aperiodicity.

There is another potential reason for deviations from the MO periodicity. Unlike the optical experiments which involve electrons with energies below and above the Fermi energy, the SdH and dHvA oscillations reflect only the properties of electrons with an energy equal to E_F. Note, that our treatment is based on the assumption that E_F is a constant. This is not quite correct as the carrier concentration is a constant and not E_F, which should oscillate as a function of B. This can be important for lowest LLs in high-mobility samples and was considered as a single source of oscillation aperiodicity in Ref. 12.

In conclusion, we have found that unlike MOs of SFs and DFs, MOs in graphite are not periodic in $1/B$. These oscillations are only asymptotically periodic in the quasiclassical limit with the phase corresponding to massive SFs. The quasiclassical limit can be reached only exceptionally for samples with very high mobility and at very low magnetic field. Therefore, the determination of the oscillation phase in samples with a limited number of resolved LLs below E_F is not a reliable tool for distinguishing between DFs and SFs in graphite, due to the aperiodicity of MOs in a standard quantum regime. Electrons in graphite are similar to SFs and DFs, as follows from Eqs. (11) and (13) but are not equivalent.

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