Quantum size effect on the paramagnetic critical field in free-standing superconducting nanofilms

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Abstract
The quantum size effect on the in-plane paramagnetic critical field in Pb(1 1 1) free-standing nanofilms is investigated with the use of the spin-generalized Bogoliubov–de Gennes equations. It is shown that the critical field oscillates as a function of the nanofilm thickness with the period $\sim 2\,\text{ML}$ (even–odd oscillations), modulated by the beating effect. The calculated values of the critical field for different nanofilm thicknesses are analyzed in the context of the Clogston–Chandrasekhar limit. It is found that the critical field for superconducting nanofilms differs from this limit. This phenomena is explained in terms of quantization of the electron energy caused by the confinement of electron motion in a direction perpendicular to the film. The thermal effect and thickness-dependence of electron–phonon coupling on the value of the critical magnetic field are also studied.

Keywords: superconducting nanofilms, quantum size effect, metallic nanofilms

(Some figures may appear in colour only in the online journal)

1. Introduction
The interplay between superconductivity and quantum confinement has attracted growing interest due to the unique phenomena that appear if the electron motion is limited to a size smaller than the coherence length [1–8]. The huge progress in nanotechnology that has been made in the last decade allows to prepare uniform ultrathin films [9–12] in which new superconducting properties have been observed. One of these properties is oscillations of the superconducting energy gap as a function of the nanofilm thickness as predicted by Blatt and Thompson [13] in 1963. The authors of [13] showed that the quantum-well states created due to the confinement of the electron motion in a direction perpendicular to the film greatly modulate the density of states near the Fermi level and thus affect the superconducting energy gap of the nanofilm. As a result, one would expect a significant increase of the energy gap each time the bottom of a sub-band passes through the Fermi sphere. However, either the experimental studies carried out in these years did not exhibit such an effect or the observed oscillations differed quantitatively from the theoretical predictions [14]. This inconsistency can be attributed to the technological difficulties in the preparation of uniform films, which were typically polycrystalline and contained a large number of defects. Since then, many technological obstacles have been overcome, which has reopened the issue for the quantum confinement effect on superconductivity in the nanoscale regime. Recently, Guo et al [15] fabricated ultrathin Pb films on Si(1 1 1) substrate and observed the oscillations of the critical temperature as a function of the nanofilm thickness. This phenomena has been explained in terms of quantization of the electron energy caused by the confinement of the electron motion in a direction perpendicular to the film. It has been confirmed independently by the measurement of quantum-well energies by using photoemission spectroscopy. The study of Pb nanofilms has been extended by Eom et al [16] who reported $T_c$ oscillations in epitaxially grown crystalline Pb films in the thickness range 5–18 ML. In [16], the critical temperature was measured using scanning tunneling microscopy, which allows
avoidance of ambiguities associated with the Au layer applied in the transport measurements [15]. A direct correlation between enhancement of the density of states at the Fermi level and increase of $T_c$ has been found. It is worth mentioning that all measurements of the critical temperature for Pb nanofilms have reported the same period of oscillations, equal to $\sim 2$ ML. This property, called bilayer or even–odd oscillations, has been theoretically investigated by Shanenko et al in [17] and observed in many other experiments [10, 18, 19].

The new direction of studies devoted to superconductivity in the nanoscale regime concerns the effect of quantum confinement on the superconductor to normal metal transition induced by the magnetic field. In metallic nanowires, it has been shown that a cascade of jumps in the energy gap as a function of the magnetic field occurs [20]. This effect has been explained in terms of depairing in the subsequent layers when the magnetic field increases [20]. Moreover, the oscillations of the perpendicular upper critical field in ultrathin lead films were reported by Bao et al in [21]. To our knowledge, the theoretical study of the superconducting to normal metal transition induced by the in-plane magnetic field and its interplay with quantum confinement has not been reported until now.

In the present paper, we investigate the superconductor-normal metal transition driven by the in-plane magnetic field for free-standing Pb(1 1 1) nanofilms. It has been found that the critical field oscillates as a function of the nanofilm thickness with the period $\sim 2$ ML (even–odd oscillations) modulated by the beating effect with periodicity 10 ML. The calculated values of the critical field for different nanofilm thicknesses are analyzed in the context of Clogston–Chandrasekhar limit. We find that the Clogston–Chandrasekhar formula cannot be used to predict the critical field in the paramagnetic limit for superconducting nanofilms. A new formula for the paramagnetic critical field in the nanoscale regime is proposed. Finally, we take into account the oscillatory behavior of electron–phonon coupling and calculate $H_{c1}$ as a function of the nanofilm thickness for the experimental samples, for which good agreement of theory and experiment has been found in the study of critical temperature [22]. The present paper is organized as follows. In section 2, we introduce the basic concepts of the calculation scheme based on the Bogoliubov–de Gennes equations. In section 3, we analyze the results, and a summary is given in section 4.

2. Theoretical method

The superconducting properties of the conventional phonon-mediated pairing system can be described with BCS theory, which leads to the Bogoliubov–de Gennes (BdG) equations in the form

$$
\begin{pmatrix}
H_{\sigma}^0 & \Delta & 0 & 0 \\
\Delta^* & -H_{\sigma}^0 & 0 & 0 \\
0 & 0 & H_{\sigma}^0 & \Delta \\
0 & 0 & \Delta^* & -H_{\sigma}^0
\end{pmatrix}
\begin{pmatrix}
U_{\sigma}^i \\
V_{\sigma}^i \\
U_{\sigma}^i \\
V_{\sigma}^i
\end{pmatrix}
= E_i
\begin{pmatrix}
U_{\sigma}^i \\
V_{\sigma}^i \\
U_{\sigma}^i \\
V_{\sigma}^i
\end{pmatrix},
$$

(1)

where $U_{\sigma}^i$ and $V_{\sigma}^i$ are the spin-dependent electron-like and hole-like wave functions ($\sigma = \uparrow, \downarrow$), $\Delta$ is the superconducting energy gap, and $E_i$ is the quasi-particle energy. In the presence of the in-plane magnetic field $H_{||}$, the Hamiltonian $H_{\sigma}^0$ is given by

$$
H_{\sigma}^0 = \frac{1}{2m} \left( -i \hbar \nabla - \frac{e}{c} A \right) \sigma^2 + s \mu_B H_{||} - \mu_F.
$$

(2)

where $s = +1$ corresponds to the spin $\sigma = \uparrow$, $s = -1$ is related to the spin $\sigma = \downarrow$, $m$ is the electron mass, $\mu_B$ is the Bohr magneton, $\mu_F$ is the chemical potential, and $A$ is the vector potential related to the parallel magnetic field.

In the present paper, we neglect the orbital effects and consider the superconducting nanofilms in the clean paramagnetic limit. This approximation is justified for nanofilms with thickness less than the magnetic length $a_H = \sqrt{\hbar/eH_{||}}$. The use of the Clogston–Chandrasekhar paramagnetic field for Pb $H^{CC} = 13.4$ T gives $a_H = 7$ nm, which means that the paramagnetic approximation can be used for Pb nanofilms with thickness less than $\sim 25$ ML (we assume the lattice constant for Pb, $a = 0.286$ nm). In the paramagnetic limit, the Hamiltonian can be further simplified to the form

$$
H_{\sigma}^0 = -\frac{\hbar^2}{2m} \nabla^2 + s \mu_B H_{||} - \mu_F.
$$

(3)

For strong Pauli limited superconductors in parallel magnetic fields, an unconventional superconducting state (FFLO) with non-zero momentum of the Cooper pairs can be created [23, 24]. In the FFLO state, the energy gap is not uniform but varies spatially with the period corresponding to the Cooper pair momentum. However, in spite of many theoretical studies [25–28], experiments indicate the possible existence of the FFLO state only in the heavy fermion system [29] and two-dimensional organic superconductors [30]. This is believed to be because the FFLO state is easily destroyed by nonmagnetic impurities [31, 32] (in contrast to the BCS state). So far there have been no reports on the non-zero momentum pairing in metallic nanofilms. For this reason, we neglected the existence of the FFLO state in our analysis and assume that the energy gap in the $x–y$ plane is homogeneous. Then, the quasi-particle wave functions can be expressed as

$$
\begin{pmatrix}
U_{\sigma,i}^0(r) \\
V_{\sigma,i}^0(r)
\end{pmatrix}
= \frac{e^{ik_{\sigma,i}z}}{\sqrt{L_z}} \frac{1}{\sqrt{L_y}} \begin{pmatrix}
\bar{u}_\sigma(r) \\
\bar{v}_\sigma(r)
\end{pmatrix},
$$

(4)

where $\bar{\sigma}$ denotes spin opposite to $\sigma$. In equation (4), the index $i$ has been replaced by $k_x, k_y$, $\nu$, where $k_x, k_y$ are the electron wave vector components in the $x$ and $y$ direction and $\nu$ labels the quantum states in the $z$ direction. By substituting the wave function given by (4) into the BdG equations (1), we obtain two independent set of equations

$$
\begin{pmatrix}
H_{\sigma}^0(z) & \Delta(z) \\
\Delta(z) & -H_{\sigma}^0(z)
\end{pmatrix}
\begin{pmatrix}
U_{\sigma,i}^0(z) \\
V_{\sigma,i}^0(z)
\end{pmatrix}
= E_i
\begin{pmatrix}
U_{\sigma,i}^0(z) \\
V_{\sigma,i}^0(z)
\end{pmatrix},
$$

(5)

and

$$
\begin{pmatrix}
H_{\sigma}^0(z) & \Delta(z) \\
\Delta(z) & -H_{\sigma}^0(z)
\end{pmatrix}
\begin{pmatrix}
U_{\sigma,i}^0(z) \\
V_{\sigma,i}^0(z)
\end{pmatrix}
= E_i
\begin{pmatrix}
U_{\sigma,i}^0(z) \\
V_{\sigma,i}^0(z)
\end{pmatrix},
$$

(6)
where
\[
H^\sigma(z) = \frac{-\hbar^2}{2m} \frac{d^2}{dz^2} + \frac{\hbar^2 k^2}{2m} + s\mu_B H|| = \mu_F
\]  
(7)

and \(k^2 = k_x^2 + k_y^2\). Assuming that the system is infinite in the \(x\) and \(y\) direction \((L_x, L_y \to \infty)\), the order parameter \(\Delta(z)\) can be expressed as

\[
\Delta(z) = \frac{g}{2\pi} \int dk_|| \int d\nu \sum_\sigma \left\{ u^{\sigma \ast}_v(z) v^{\sigma}_v(z) \left[ 1 - f(E^\ast_v) \right] + u^{\sigma}_v(z) v^{\sigma \ast}_v(z) f(E^\ast_v) \right\},
\]  
(8)

where \(g\) is the electron–phonon coupling and \(f(E)\) is the Fermi–Dirac distribution. The summation in equation (8) is carried out only over the single-electron states with energy \(\xi_{k_\parallel,\nu}^\sigma < \hbar \omega_D\), where \(\omega_D\) is the Debye frequency and \(\xi_{k_\parallel,\nu}^\sigma\) is given by

\[
\xi_{k_\parallel,\nu}^\sigma = \int_0^d dz \left\{ u^{\nu \ast}_v(z) H^\sigma(z) u^{\nu}_v(z) + v^{\nu \ast}_v(z) H^\sigma(z) v^{\nu}_v(z) \right\},
\]  
(9)

where \(d\) is the nanofilm thickness in the \(z\)-direction. The above condition comes from the BCS theory and results from the delta-function approximation for the effective electron–electron interaction mediated by phonons [33]. The system of equations (5)–(6) and equation (8) are solved in a self-consistent manner. As a result, the spatially varying energy gap \(\Delta(z)\) is obtained. In the further analysis we often use spatially averaged energy gap defined as

\[
\bar{\Delta} = \frac{1}{d} \int \Delta(z) dz.
\]  
(10)

Since the chemical potential for nanostructures strongly deviates from the bulk value, for each nanofilm thickness, we determine the chemical potential by using the formula

\[
n_e = \frac{1}{\pi d} \int dk_|| \sum_\nu \int_0^d dz \left\{ |u^{\nu}_v(z)|^2 f(E_v) + |v^{\nu}_v(z)|^2 [1 - f(E_v)] \right\}.
\]  
(11)

In our calculations, we apply the hard-wall potential profile as the boundary conditions in the \(z\) direction. The set of self-consistent equations can lead to solutions with \(\Delta \neq 0\), even for the values of the magnetic field for which the superconducting phase is already unstable; its free energy is greater than the free energy corresponding to the normal metal solution \((\Delta = 0)\). This is why, when determining the critical field, one should calculate and compare the free energy of the normal and superconducting phase, as done here.

3. Results

In this section, we analyze the superconductor to normal metal transition induced by the parallel magnetic field. The thickness range under consideration was chosen based on the experiments for Pb(1 1 1) nanofilms with thicknesses varying from 5 ML to 30 ML [15, 16]. The calculations were carried out for the following values of the parameters: \(gN_{\text{bulk}}(0) = 0.39\) where \(N_{\text{bulk}}(0) = mk_B/(2\pi^2\hbar^2)\) is the bulk density of the single-electron states at the Fermi level, \(\hbar \omega_D = 8.27\) meV, the lattice constant \(a = 0.286\) nm, and the bulk critical temperature \(T_{\text{bulk}} = 7.2\) K, which corresponds to the energy gap \(\Delta_{\text{bulk}} = 1.1\) meV. Despite the fact that the phonon dispersion in thin films deviates from that in the bulk, we assume the bulk value of the parameter \(\hbar \omega_D\) in our analysis. The reason for this is our additional calculations, which show that the results presented in the paper are only slightly affected by changes in this parameter’s values. A much more important effect is related to the changes in the electron–phonon coupling caused by the interface. This effect is considered in detail in section 3.3. Since the diffraction measurements indicate that the in-plane lattice constant \(a\) is close to the bulk value, we assume \(a = 0.286\) nm, corresponding to that measured in the bulk.

For quantitative description of the quantum size effect in nanofilms, the actual band structure from \textit{ab-initio} calculations is needed. The first-principle calculations of the quantized band structure for Pb nanofilms in (1 1 1) and (1 0 0) directions are presented in [34–36], where the oscillations of the work function and the surface energy are studied. It has been found [35] that the proper determination of the oscillation period for Pb(1 0 0) films requires taking into account the quantum wall states centered at \(\Gamma\) and \(M\) points in the two-dimensional Brillouin zone. On the other hand, the calculations show that the quantum size effect in Pb(1 1 1) films can be well described, even if one takes into account only the quantum well states centered at the \(L\) point [34]. In this direction, the energy dispersion is nearly parabolic. Based on these results, in the present paper (we consider Pb(1 1 1)) we use the parabolic band approximation, treating the bulk Fermi level and electron mass as the fitting parameters. Their values are determined in such a way as to reproduce the results of the first-principle calculations for Pb(1 1 1) from [34]. We take on \(\mu_{\text{bulk}} = 3.8\) eV, which corresponds to the \(n_e = 4.2 \times 10^{21}\) cm\(^{-3}\) and \(m = 0.25m_0\), where \(m_0\) is the free electron mass.

3.1. Paramagnetic critical field oscillations

In figure 1, the in-plane critical field \(H_{c||}\) as a function of the nanofilm thickness is presented for different temperatures \(T\). The value of \(H_{c||}\) is determined based on calculations of the energy gap versus the magnetic field and is defined as the field for which the spatially averaged energy gap \(\bar{\Delta}\) drops below 0.01\(\Delta_{\text{bulk}}\). Figure 1(a) shows that the paramagnetic critical field oscillates with the period of 2 ML. The difference between 2 ML and the real period of the quantum well states that pass through the Fermi surface results in the beating effect with the periodicity of 10 ML. Even–odd (bilayer) oscillations with the beating effect have been observed in recent measurements of the critical temperature [15, 16] and electron–phonon coupling in Pb thin nanofilms [10]. In these experiments, the modulation periodicity varies from 7 ML [16] to 9 ML [37], indicating that this quantity depends on the quality of the nanofilm and might vary from one experiment to another. The oscillations of \(H_{c||}\) in figure 1 result from the
Figure 1. In-plane critical magnetic field $H_{c,||}$ as a function of the nanofilm thickness $d$ calculated for the temperature (a) $T = 0$ K, (b) $T = 6$ K, and (c) $T = 8$ K. Results for even-layered nanofilms are marked by triangular red points and for odd-layered nanofilms by square blue points. (d) Chemical potential $\mu$ as a function of the nanofilm thickness $d$.

Figure 2. Zero temperature spatially averaged energy gap $\bar{\Delta}/\Delta_1$ as a function of the nanofilm thickness $d$. Results for even-layered nanofilms are marked by triangular red points and for odd-layered nanofilms by square blue points. The green horizontal line denotes the value of the energy gap in the bulk.

The confinement of the electron motion in a direction perpendicular to the film. The confinement of the electron motion leads to the quantization of its energy. The Fermi sphere transforms into a series of parabolic subbands, positions of which on the energy scale decreases with increasing nanofilm thickness. Since the Cooper-pairing in the phonon-mediated superconductor is determined by the number of the electron states in the energy window $[\mu - \hbar \omega_D, \mu + \hbar \omega_D]$ ($\hbar \omega_D$ is Debye energy), the superconducting energy gap increases each time the subsequent subband passes through the Fermi surface. The presented mechanism, predicted theoretically in 1963 by Blatt and Thomson [13], results in tooth-like oscillations of the spatially averaged energy gap $\bar{\Delta}$ as a function of the nanofilm thickness. The tooth-shape of the energy gap oscillations is directly related to changes of the electron density of states in the vicinity of the Fermi level. It abruptly increases when the sub-band minima reach the Fermi level and then exponentially decreases with increasing nanofilm thickness [13]. The zero temperature energy gap $\bar{\Delta}$ as a function of the number of monolayers is presented in figure 2. One can see that the shape of $H_{c,||}$ oscillations at $T = 0$ K (figure 1(a)) is strongly correlated with the shape of $\Delta$ oscillations in figure 2. The reason for is due to the fact that in the ultra thin nanofilms with in-plane magnetic field, the pair-breaking mechanism is mainly governed by the paramagnetic (Pauli) limit, which is given by the Clogston–Chandrasekhar (CC) formula, $H_{\text{CC}} = \Delta_{\text{bulk}}/(\sqrt{2}\mu_B)$. Therefore, the bilayer oscillations of the in-plane critical field presented in figure 1(a) are caused by the contribution of the subsequent sub-bands, which increases
Figure 3. Quasi-particle energy $E$ as a function of the wave vector $k$ for the film thickness (a) $d = 5$ ML, (b) $d = 6$ ML, (c) $d = 8$ ML, and (d) $d = 9$ ML.

The density of states at the Fermi level. In figure 3, the quasi-particle energy $E$ versus the wave vector $k$ is presented for the film thickness $d = 5, 6$ ML (a, b) and $d = 8, 9$ ML (c, d). The first pair of thicknesses correspond to the range in which $H_{c\parallel}$ is higher for the even-layered films, while the second pair is related to the range for which a reversed situation is observed. We see that for the film thickness $d = 5$ ML, the two lowest sub-bands participate in the creation of the superconducting state (figure 3(a)). Increasing the thickness by one monolayer causes the third subband to begin to contribute to the superconducting phase, which leads to the enhancement of the critical field depicted in figure 1(a). In the thickness range 3–7 ML, the subsequent sub-bands pass through the Fermi level only if the number of monolayers is even. The period of the passages can be well estimated by the single-electron energy level in the form $E \approx \hbar^2 \pi^2 \nu^2 / (2md^2)$, where the hard-wall potential is assumed in the $z$ direction. The difference between 2 ML and the real period of the quantum well states that pass through the Fermi surface ($\Delta d = 2.2$ ML) results in the beating effect observed in figure 1(a). This is the reason why, in figures 3(c) and (d), the new subband ($\nu = 4$) appears for the odd-layered film ($d = 9$ ML), in contradiction to the pair $d = 5, 6$ ML (see figures 3(a) and (b)). The source of the beating effect is clearly visible in figure 4, where the energy of the quantum well states as a function of nanofilm thickness is presented.

Figure 4. Energy of the quantum well states $E_{QW}$ as a function of film thickness $d$. Results for even-layered nanofilms are marked by triangular red points and for odd-layered nanofilms by square blue points. The Fermi level $\mu$ is set to zero. The energy closest to the Fermi level is joined by the blue (red) line for the even (odd) number of monolayers.

In figure 4, only the states with energy below Fermi level (set as zero energy) are occupied and contribute to the Cooper pair condensation. The closer they are located to the Fermi
energy, the larger their contribution to the density of states at the Fermi level and, consequently, Cooper pairing. In figure 4, the energies closest to the Fermi level are joined by the blue (red) line for the even (odd) number of monolayers. Note that such a procedure leads to the 'structure' (in the sense of the shape) exactly the same as depicted in figure 1(a).

Let us now discuss the value of the paramagnetic critical field obtained from our calculations in the context of the Clogston–Chandrasekhar limit. It is well-known that in ultra thin films with an in-plane magnetic field, the orbital-magnetic interaction is strongly reduced and the upper limit of the critical field is determined by the paramagnetic breakdown of the Cooper pairs. For the bulk energy gap $\Delta_{1Pb}$, the CC formula gives $H_{CC}^{Pb} = 13.4$ T. This value strongly differs from the critical field obtained in our calculations that vary from 15 T to 30 T. Such deviation for Pb nanofilms was reported recently in [40], where the experimentally measured critical field $H_{c,||}$ was much higher than the paramagnetic limit $H_{CC}$. It seems that such discrepancy results from the enhancement of the energy gap presented in figure 2. Nevertheless, the use of the CC formula with the spatially averaged energy gap calculated for each nanofilm thickness $H_{CC}^{S} = \Delta(d)/(\sqrt{2}\mu_B)$ still produces the value of the critical field, which is lower than the results from numerical solution of the spin-generalized BdG equations, i.e. for $d = 6$ ML, $H_{CC}^{S} = 24.5$ T, while calculated $H_{c,||} = 28.5$ T. This fact can be easily understood if we realize that the superconducting energy gap depends on the $z$ coordinate and is not uniform as in the expression for the CC critical field. Taking into account the correction resulting from the averaging of the energy gap over the $z$ coordinate, we introduce the thickness-dependent parameter $\alpha(d)$ and propose the expression for the critical field in the form

$$H_{c,||} = \alpha(d) \frac{\Delta(d)}{\mu_B}. \quad (12)$$

Figure 5 shows that the parameter $\alpha$ is the decreasing function of thickness $d$ and, for sufficiently large thickness, reaches the value $\alpha = 1/\sqrt{2}$. The asymptotic behavior of $\alpha(d)$ for $d \to \infty$ results from the fact that, for a large thickness, the spatially varying energy gap diverges to the uniform one. Compare $\Delta(z)$ for the thicknesses $d = 4$ and 20 ML presented in the inset of figure 5. The dependent $\alpha(d)$ can be well fitted using the formula $\alpha = A/d + 1/\sqrt{2}$, where the thickness $d$ denotes the number of monolayers (see figure 5). It should be noted that the smallest difference between the quasiparticle energy in the superconducting state and the Fermi energy is the same for each band created, due to the confinement of electrons in a direction perpendicular to the sample (see figure 3). Using this energy gap instead of the averaged energy gap $\Delta$ in the CC formula, one obtains the same values of critical fields as those resulting from the BdG equations.

3.2. Thermal effect

In the present subsection, we discuss in detail the effect of temperature on the superconductor to normal metal transition induced by the in-plane magnetic field. The critical field $H_{c,||}(d)$ presented in figure 1 for different temperatures $T$ shows that its value gradually decreases with increasing temperature. Since the critical temperature oscillates as a function of nanofilm thickness (similar to the energy gap depicted in figure 2), at the temperature $T = 8$ K, the nanofilms with thickness $d = 7, 9$ ML are superconducting, while the film with thickness in between transits to the metallic state.

In figure 6, we present the spatially averaged energy gap $\Delta$ as a function of the magnetic field $H$ and temperature $T$ for nanofilms thicknesses (a) $d = 5$ ML, (b) $d = 6$ ML, (c) $d = 8$ ML, and (d) $d = 9$ ML. The value of the energy gap in each figure is normalized with respect to its maximum.

![Figure 5. $\alpha$ as a function of the film thickness $d$. The red line is the fitting curve in the form $\alpha = A/d + 1/\sqrt{2}$, $A = 0.85$. The inset: the spatially varying energy gap $\Delta(z)$ calculated for the nanofilm thicknesses $d = 4$ ML and $d = 20$ ML.](image1)

![Figure 6. Spatially averaged energy gap $\Delta$ as a function of the magnetic field $H$ and temperature $T$ for nanofilms thicknesses (a) $d = 5$ ML, (b) $d = 6$ ML, (c) $d = 8$ ML, and (d) $d = 9$ ML. The value of the energy gap in each figure is normalized with respect to its maximum.](image2)
with respect to its maximum. In figure 6, we can see that the range of the magnetic field and temperature for which the sample is superconducting is larger for the thickness for which the enhancement of the energy gap (see figure 2) is found. Nevertheless, the thickness-dependence is not visible which the enhancement of the energy gap (see figure 2) is found. In this range, the transition at $H = 0$ and the critical temperature for $H = 0$, respectively. In other words, the phase diagram $h - t$ presented in figure 7 looks the same for each film thickness, which is understandable if we recall our restriction to the Pauli limit with no orbital effect. The initial behavior of $h$ at a temperature close to $T_c$ ($t = 1$) can be well estimated by the formula $h = A(1 - t)^{1/2}$. Note that, in contrast to the orbital limit with no Pauli effect, the slope of $h$ at critical temperature $t = 1$ is infinite and in the vicinity of $t = 1$ is expressed by $dh/dt \propto \sqrt{T}(1 - t)$. In this range, the transition at $H_{c\parallel} = 0$ is of second order. In the Pauli limit, the second order transition is suppressed with decreasing temperature and below $t^* = 0.56$ becomes first order [41, 42]. The first to second order transition is clearly presented in figure 8, where the energy gap versus magnetic field is presented for different temperatures. Note that the critical field $H_{c\parallel} = 0$ at $T = 0$ is not equal to the paramagnetic limit $H_{c\parallel}^{CC}$ but is further enhanced. A detailed discussion of the deviation of the critical field from $H_{c\parallel}^{CC}$ is presented in section 3.1.

### 3.3. Thickness dependent electron–phonon coupling

The microscopic model based on the spin-generalized BdG equations allows us to analyze the superconductor to normal metal transition in nanofilms when their thickness is reduced to a few nanometers. However, in the nanoscale regime, the confinement affects not only the electronic spectrum, but also the phononic degrees of freedom. The phonon dispersion in thin films strongly deviates from that in the bulk [43]. The quantization of the phononic spectra in nanofilms and its influence on $T_c$ and energy gap oscillations are considered in [44]. However, the effect of the confinement on electron–phonon coupling strength was not included. This lack has been recently supplemented by Saniz et al. [45]. In this paper, the authors have investigated the effect of confinement on the strength of electron–phonon coupling as well as the electronic spectrum and its influence on oscillations of the critical temperature. The formula for the phonon-mediated attractive electron–electron interaction was derived using the Green function approach beyond the contact potential approximation. It has been found that the increase of the critical temperature observed in superconducting nanofilms is due to the increase of the number of phonon modes, which results in the enhancement of electron–phonon coupling. In contradiction to previous models [7, 17], this study predicts the suppression of the critical temperature with increasing density of states at the Fermi level. Such conclusion seems not to be confirmed by recent experiments in which the direct correlation between the $T_c$ oscillations and energy distribution of the quantum well states in nanofilms was observed [16].

To determine the realistic value of the electron–phonon coupling that occurs in experiments, there is one more aspect that should be taken into consideration. Note that the results presented in this paper regard so-called freestanding nanofilms. In fact, Pb films are grown on Si(1 1 1) substrate and, for the purpose of transport measurements, are covered by a layer of Au. Both these layers strongly affect the electron–phonon coupling in nanofilms due to the interface effect. It has been observed recently [37] that the electron–phonon coupling for Pb nanofilms on Si substrate is lower than in the bulk and

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**Figure 7.** Critical field $h = H_{c\parallel}/H_{c\parallel}(0)$ as a function of $t = T/T_c(0)$ obtained from the solution of BdG equations. Here, the dashed green line corresponds to $h = 1.52(1 - t)^{1/2}$. The first to second order transition, $t^*$, is marked by the arrow.

**Figure 8.** Spatially averaged energy gap $\bar{\Delta}$ as a function of magnetic field $H$ for different temperatures. The first to second order transition emerges at $t = t^* = 0.56$. Calculations performed for the film thickness $d = 10$ ML.

**Table 1.** The value of parameters used in reference [22] to reproduce the oscillations of $T_c$ observed in experiments—see reference column.

| Reference | $g_0 N(0)$ | $g_1(\pi)$ | $g_2(2\pi)$ |
|-----------|------------|------------|------------|
| [16]      | 0.36       | -0.12$b_0$ | 0.84$b_0$  |
| [18]      | 0.39       | 0.64$b_0$  | 1.46$b_0$  |
| [46]      | 0.39       | 1.67$b_0$  | 2.13$b_0$  |
diverges to the bulk value with increasing film thickness. The results presented in [37] indicate that the interface effect has a strong impact on the electron–phonon coupling and should be taken into account in the presented model in order to reproduce the experimental data. The simple approximation that allows us to take this effect into account was recently proposed by Chen et al in [22]. It is assumed [22] that in the first approximation, spatially-dependent electron–phonon coupling can be well estimated by the formula

$$g(z) = \begin{cases} 
g_{if} & 0 < z < d_{if} \\
g_0 & d_{if} < z < d 
\end{cases}$$  \hspace{1cm} (13)

where $d_{if}$ is the interface thickness with electron–phonon coupling $g_{if}$, and $g_0$ is electron–phonon coupling in the bulk. Averaging over the $z$ coordinate and including the oscillatory behavior of $g$ coefficient reported in experiments [37] leads to the formula (for details see [22])

$$\tilde{g} = g_0 - \frac{g_1}{N} \left( \frac{4\piaN}{\lambda} \right),$$  \hspace{1cm} (14)

where $g_1(x)$ is a periodic function, $N$ is the number of monolayers, $\lambda_F$ is the Fermi wavelength, and $a$ is the lattice constant. Since the period of $T_c$ oscillations in Pb nanofilms is measured to be $\sim 2\text{ML}$, the authors of [22] reduced the function $g_1(x)$ to only two parameters: $g_1(\pi)$ for an odd number of monolayers and $g_1(2\pi)$ for an even number of monolayers. By appropriate choice of these parameters and by setting the Fermi level to the value corresponding to the period of the quantum-size oscillations (2 ML), one can well reproduce the experimental data of $T_c(d)$ from [16, 18, 46]. The values of the parameters used for each of the mentioned references is presented in table 1.

In the present subsection, we use these parameters to predict the zero temperature in-plane critical field as a function of nanofilm thickness. We believe that this procedure allows us to determine the realistic value of the critical field that is comparable with recent experimental measurements [40]. The thickness-dependent oscillations of the zero temperature critical field are presented in figure 9. Although the periodicity of the $H_{c||}$ oscillations for each of the considered references is the same and equals 2 ML, the characteristics of these oscillations are different and vary by experiment. This difference regards the overall trend of $H_{c||}$, which is an increasing function of thickness in the case of [18, 46] but decreasing in the case of [16]. Note that the values of the critical field in figure 9 are suppressed compared to the critical field calculated with electron–phonon coupling for the bulk (compare with figure 1(a)).

4. Summary

The superconductor to normal metal phase transition driven by the magnetic field for Pb nanofilms is investigated with the use of the BdG equations. Only the Pauli pair-breaking mechanism is included as it is assumed that the external magnetic field is parallel to the surface of the nanofilm. It is shown that even–odd oscillations of the critical magnetic field appear as the thickness of the sample is increased. The shape of the $H_{c||}$ oscillations is directly related to the shape of the thickness dependence of the superconducting gap. The beating effect visible in the oscillations is discussed in the context of the energy of the quantum well states and appears to be due to the confinement of the electron motion in the direction perpendicular to the sample. As illustrated, the period in the nanofilm thickness between two neighboring peaks in the critical field is equal to 2.2 ML. As the number of monolayers must be an integer, the beating effect appears in the oscillatory behavior of $H_{c||}$ and $\Delta$. We also show that the zero-temperature critical field in nanofilms is higher than the Clogston–Chandrasekhar paramagnetic limit and diverges to the CC value for sufficiently thick films. This fact is explained in terms of the spatially varying energy gap induced by the confinement. The phase diagrams in the $(H, T)$ plane are presented for different values of $d$. According to the obtained results, the thickness-dependence is not visible in the phase diagrams when both the field and the temperature are normalized $h = H_{c||}/H_{c||}(0)$ and $t = T/T_c(0)$. Moreover, the interface effect on the electron–phonon coupling is included using a simple approximation proposed in [22]. This leads to a spatially dependent $g$ factor and its oscillatory behavior with increasing nanofilm thickness. As shown, this effect leads to a suppression of the critical field values in comparison to those corresponding to the bulk. We believe that such an approach allows for comparison of the calculated $H_{c||}$ oscillations with the experimental results.
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