

Influence of the electron density on the thickness-dependent energy gap oscillations in superconducting metallic nanofilms

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The thickness-dependent energy gap oscillations in the metallic nanofilms are investigated by the use of the self-consistent numerical solutions of the Bogoliubov-de Gennes equations. We analyze, how the changes in the electron density (n_e) and the electron-phonon coupling constant (g) influence the amplitude of the considered oscillations.

It is found, that the increase in n_e and the decrease in g can lead to a significant reduction of the oscillations amplitude. As a result, for the values of the mentioned parameters which correspond to some of the realistic situations the thickness-dependent superconducting gap oscillations can be significantly suppressed. The computational results are compared with recent experimental data.

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1 Introduction The huge progress in nanotechnology which has been made in the last decade allows for the fabrication of high quality metallic nanostructures, e.g., metallic nanowires [1–4] and nanofilms with thickness of a few monolayers [5–12]. When the miniaturization reaches the level for which the size of the nanostructure becomes smaller than the phase coherence length ξ , the superconducting properties of the system start to deviate significantly from those in the bulk. The distinctive experimental manifestation of the size effect is the non-zero resistance below T_C observed in the quasi-1D superconducting wires [13,14,2]. Such unusual behavior results from the phase fluctuations which occur when the diameter of the nanowire is reduced to tens of nanometer [15–17]. In the nanoscale regime the superconducting properties of the system change also due to the simple fact, that the reduction of the electron motion results in the quantization of its energy. In consequence, the Fermi sphere splits into a se-

ries of subbands. Energies which correspond to those subbands are increasing as the electron motion is being limited. Since the superconducting properties depend strongly on the density of states around the Fermi surface, the superconducting gap of a metallic nanostructure drastically changes each time a subsequent subband pass through the Fermi level. The size-dependent enhancement of the energy gap induced by the quantum size effect has been theoretically investigated by Shanenko et al. in Refs. [18,19], for Al and Sn nanowires. Within these studies the experimentally observed width-dependent increase of T_C for Al nanowires [1,20] has been reproduced.

The oscillations of the superconducting gap as a function of the thickness in ultrathin nanofilms have been predicted by Blatt and Thomson [21]. During recent years superconducting nanofilms have attracted growing interest. One should also note that studies have been made regarding superconducting superlattices for both conven-

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tional (BCS) [22] and high-Tc materials [23]. Although it was expected that the quantum size effect in the superconducting nanofilms would not be an important factor (as the size reduction concerns only one dimension), recent experiments for Pb nanofilms [5,8] grown on a Si(111) substrate have shown, that the critical temperature and the critical magnetic field oscillate as a function of the nanofilm thickness. Furthermore, it has been found that the superconducting phase of the nanofilm is not destroyed by the fluctuations even if the nanofilm is only one monolayer thick [11]. The oscillations of the superconducting gap as a function of the thickness for Pb nanofilm have been studied theoretically in Ref. [24]. In these considerations the effective Fermi level has been introduced in order to reproduce the experimental results. Such fitting method leads to a situation in which the effective Fermi level used in the calculations is almost an order of magnitude smaller than the one measured in the bulk. It means that the electron density in the nanofilm has been reduced by a few orders of magnitude as compared to the electron density usually measured in metals. Intrigued by this discrepancy, in the present paper, we study the influence of the electron density on the thickness-dependent superconducting gap oscillations for the metallic nanofilms. First, we use the effective value of Fermi level and show that the quantum size effect leads to the oscillations of the order parameter as a function of the nanofilm thickness. For sufficiently thin nanofilms, with thickness of 1-2 nm, the order parameter reaches value which is five times higher than the one corresponding to the bulk. In the next step, we perform our analysis for different electron densities (Fermi levels) and find that the amplitude of the energy gap oscillations decreases with increasing electron density. We show that the amplitude reduction is significant for the electron density corresponding to that measured in metals. Finally, the thickness-dependent oscillations of the superconducting gap are also studied as a function of the electron-phonon coupling.

The present paper is organized as follows. In Sec. 2 we introduce the basic concepts of the calculation scheme based on the BdG equations. In Sec. 3 we analyze the results, while the conclusions and summary are included in Sec. 4.

2 Theory The microscopic theory based on the Bogoliubov-de Gennes (BdG) equations is a natural way to describe the superconducting properties of nanofilms in which the quantum size effect entails the position-dependent order parameter $\Delta(z)$. The BdG equations have the form

$$\begin{pmatrix} -\frac{\hbar^2}{2m}\nabla^2 - \mu & \Delta(\mathbf{r}) \\ \Delta(\mathbf{r}) & \frac{\hbar^2}{2m}\nabla^2 + \mu \end{pmatrix} \begin{pmatrix} \mathcal{U}_i(\mathbf{r}) \\ \mathcal{V}_i(\mathbf{r}) \end{pmatrix} = E_i \begin{pmatrix} \mathcal{U}_i(\mathbf{r}) \\ \mathcal{V}_i(\mathbf{r}) \end{pmatrix}, \quad (1)$$

where $\mathcal{U}_i(\mathbf{r})$ and $\mathcal{V}_i(\mathbf{r})$ are the electron-like and hole-like wave functions, E_i is the quasi-particle energy, m is the free electron mass, μ is the chemical potential, and $\Delta(\mathbf{r})$

is the position-dependent order parameter, which in the absence of the magnetic field, is a real quantity.

Assuming the periodic boundary conditions in the $x - y$ plane, the quasi-particle wave functions can be expressed as

$$\begin{pmatrix} \mathcal{U}_{k_x k_y \nu}(\mathbf{r}) \\ \mathcal{V}_{k_x k_y \nu}(\mathbf{r}) \end{pmatrix} = \frac{e^{ik_x x}}{\sqrt{L_x}} \frac{e^{ik_y y}}{\sqrt{L_y}} \begin{pmatrix} u_\nu(z) \\ v_\nu(z) \end{pmatrix}. \quad (2)$$

In the above equation, the index i has been replaced by $\{k_x, k_y, \nu\}$, where k_x, k_y are the free electron wave vector components in the x and y direction, respectively while ν labels the subsequent quantum states in the z direction.

By substituting the wave function given by (2) into the BdG equations we obtain

$$\begin{pmatrix} H_e(z) & \Delta(z) \\ \Delta(z) & -H_e(z) \end{pmatrix} \begin{pmatrix} u_\nu(z) \\ v_\nu(z) \end{pmatrix} = E_\nu \begin{pmatrix} u_\nu(z) \\ v_\nu(z) \end{pmatrix}, \quad (3)$$

where $k_\parallel^2 = k_x^2 + k_y^2$ and

$$H_e(z) = -\frac{\hbar^2}{2m} \frac{d^2}{dz^2} - \mu + \frac{\hbar^2 k_\parallel^2}{2m}. \quad (4)$$

If we assume that the system is infinite in the x and y direction ($L_x, L_y \rightarrow \infty$), the order parameter $\Delta(z)$ can be expressed in the following manner

$$\Delta(z) = \frac{g}{2\pi} \int dk_\parallel k_\parallel \sum_\nu u_\nu(z) v_\nu^*(z) [1 - 2f(E_\nu)], \quad (5)$$

where g is the electron-phonon coupling and $f(E)$ is the Fermi-Dirac distribution. The summation in Eq. (5) is carried out only over these states for which the single-electron energy $\xi_{k_x k_y \nu}$ satisfies the condition $|\xi_{k_x k_y \nu}| < \hbar\omega_D$, where ω_D is the Debye frequency and $\xi_{k_x k_y \nu}$ is given by

$$\xi_{k_x k_y \nu} = \int dz \left[u_\nu^*(z) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} - \mu + \frac{\hbar^2 k_\parallel^2}{2m} \right) u_\nu(z) + v_\nu^*(z) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} - \mu + \frac{\hbar^2 k_\parallel^2}{2m} \right) v_\nu(z) \right]. \quad (6)$$

The system of equations (3) and equation (5) are solved in a self consistent manner by using the following procedure: in the first step, we find the quasi-particle wave functions by solving the BdG equations (3) with the order parameter $\Delta(z)$ (in the first iteration we use $\Delta(z) = \Delta_{bulk}$, where Δ_{bulk} is the energy gap in the bulk). In the next step, after inserting the quasi-particle wave functions into Eq. (5), we calculate the new order parameter profile $\Delta(z)$. Using this profile, we again solve the BdG equations (3). This procedure is repeated until convergence is reached.

Since the chemical potential for the nanostructures deviates from the bulk value, for each nanofilm thickness we

determine the chemical potential using the formula

$$n_e = \frac{1}{\pi d} \int dk_{\parallel} k_{\parallel} \times \sum_{\nu} \int dz \left[|u_{\nu}(z)|^2 f(E_{\nu}) + |v_{\nu}(z)|^2 (1 - f(E_{\nu})) \right], \quad (7)$$

where d is the thickness of the film in the z direction. We use the hard-wall potential profile leading to the boundary conditions $u_{\nu}(0) = u_{\nu}(d) = 0$ and $v_{\nu}(0) = v_{\nu}(d) = 0$.

3 Results and Discussion The results presented in this section correspond to Al nanofilms and have been calculated assuming the following values of the parameters: $gN_{bulk}(0) = 0.18$ where $N_{bulk}(0) = mk_F/(2\pi^2\hbar^2)$ is the bulk density of the single-electron states at the Fermi level, $\hbar\omega_D = 32.31$ meV and the bulk energy gap $\Delta_{bulk} = 0.25$ meV. In Ref. [25,24], the Fermi level in the bulk μ_{bulk} has been treated as a fitting parameter and its value has been determined based on the experimental results from the photoemission spectroscopy, i.e., it is set to $\mu_{bulk} = 0.9$ eV, which corresponds to the electron density $n_e \approx 4 \times 10^{21} \text{ cm}^{-3}$ [18]. The electron density associated with the effective Fermi level, is an order of magnitude lower as compared to the one measured in Al bulk $n_e = 1.8 \times 10^{23} \text{ cm}^{-3}$ [26]. As it has been stated by the authors of Ref. [25], this discrepancy results from the parabolic band approximation used in the model. Nevertheless, in our opinion the extended study of the influence of the electron density on the superconducting properties of metallic nanofilms is needed and according to our knowledge, has not been reported until now. For this purpose, we first present the results of calculations carried out for the effective Fermi level and then present how the considered phenomena are changed with increasing electron density up to the value measured in the bulk.

In Fig. 1(a) we present the superconducting parameter Δ as a function of the nanofilm thickness d calculated for the effective Fermi level $\mu_{bulk} = 0.9$ eV. The dependence $\Delta(d)$ shows that for particular value of d the energy gap abruptly increases reaching the value about five times higher as compared to Δ_{bulk} [Fig.1(a)]. The oscillations of the energy gap as a function of the nanofilm thickness correspond to the confinement of the electrons in the nanofilm and can be understood in the following manner. In the superconducting state the Cooper-pairs are formed by electrons with energies from the range close to the Fermi level. This energy range is determined by the electron-phonon coupling and is limited by the Debye energy $\hbar\omega_d$, where ω_d is the Debye frequency. It means that the superconducting gap strongly depends on the number of states in the energy window $[\mu - \hbar\omega_D, \mu + \hbar\omega_D]$ around the Fermi level. In the ultra thin nanofilm, the electron motion in the direction perpendicular to the surface is limited to the nanometer size what leads to the quantization of the electron energy. In the free electron model, the Fermi sphere transforms into the series of parabolic subbands, positions of which on the

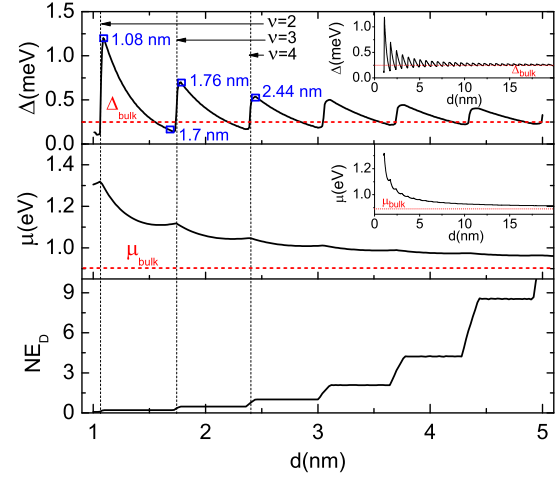


Figure 1 (a) Superconducting energy gap Δ , (b) chemical potential μ and (c) number of electronic states in the energy window $E_D = [\mu - \hbar\omega_D, \mu + \hbar\omega_D]$ as a function of the nanofilm thickness d . Internal panels present the thickness-dependencies $\Delta(d)$ and $\mu(d)$ in wider range of d varying from 1 nm up to 20 nm and clearly show that both these parameters converge to their bulk values as the nanofilm thickness increases.

energy scale decreases with increasing nanofilm thickness. If we increase the thickness d , the subsequent subbands pass through the energy window $[\mu - \hbar\omega_D, \mu + \hbar\omega_D]$ what leads to the step-like enhancement of the density of states participating in the condensation of the Cooper-pairs [see Fig. 1(c)]. The described mechanism is responsible for the increase of the energy gap Δ depicted in Fig. 1(a). As one can see the peaks in the $\Delta(d)$ dependence are accompanied by a small chemical potential increases [see Fig. 1(b)]. In Fig. 1(a) the highest enhancement of the energy gap is observed for the first three maxima, which correspond to the condensation of Cooper-pairs from the second, third, and fourth subband, respectively. In Fig. 2 we present the quasi-particle energy E and the kinetic energy ξ as a function of the wave vector k_{\parallel} for several nanofilm thicknesses: (a) $d = 1.08$ nm which corresponds to the first maximum of $\Delta(d)$, (b) $d = 1.7$ nm which corresponds to the drop of the energy gap below its bulk value, (c) $d = 1.76$ nm and (d) $d = 2.44$ nm which correspond to the second and third maximum of $\Delta(d)$. The thicknesses for which E vs k and ξ vs k dispersions have been calculated, are marked by squares in Fig. 1(a). We can see that for the nanofilm thickness $d = 1.08$ nm [see right panel in Fig.2(a)] the enhancement of the energy gap corresponds to the Cooper pairing of electrons from the subband $\nu = 2$ which minimum of the kinetic energy is located in the energy window $[\mu - \hbar\omega_D, \mu + \hbar\omega_D]$. By analogy, the analysis of Figs. 2(c) and (d) allows to conclude that the second and third maxima correspond to the condensation of electrons from the subband $\nu = 3$ and $\nu = 4$, respec-

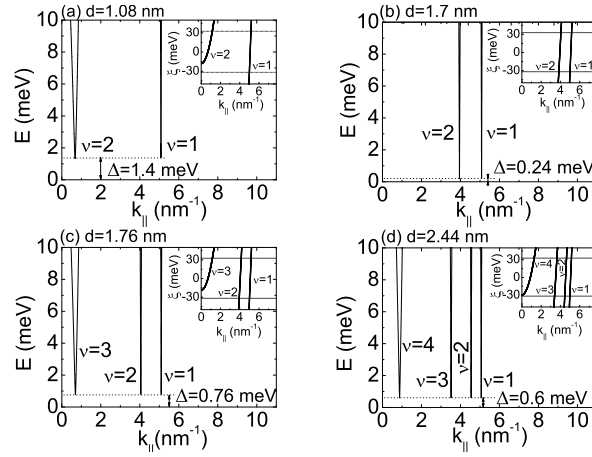


Figure 2 Quasi-particle energy E (left) and kinetic energy ξ (right) as a function of the wave vector $k_{||}$ for nanofilm thicknesses (a) $d = 1.08$ nm, (b) $d = 1.7$ nm, (c) $d = 1.76$ nm and (d) $d = 2.44$ nm [see Fig. 1(a)]. The energy window $[\mu - \hbar\omega_D, \mu + \hbar\omega_D]$ in the right panels are marked by dashed horizontal lines.

tively. In contrary, in Fig. 2(b) we can observe that the drop of the energy gap below its bulk value results from the fact that the minimum of the subband $\nu = 2$ leaves the energy window $[\mu - \hbar\omega_D, \mu + \hbar\omega_D]$. The participation of the subsequent subbands in the creation of the superconducting state leads also to the inhomogeneity of the energy gap in the z direction which is presented in Fig. 3. In this figure the number of maxima corresponds to the state number ν which is responsible for the enhancement of the energy gap. It should be noted, that the amplitude of $\Delta(d)$ oscillations in Fig 1(a) decreases with increasing nanofilm thickness, for which the higher excited states participate in the Cooper pair condensation. The internal panels of Fig. 1 present the thickness-dependencies $\Delta(d)$ and $\mu(d)$ in wider range of d varying from 1 nm up to 20 nm and clearly show that both Δ and μ converge to their bulk values as the nanofilm thickness increases.

As it can be seen, within the considered model, with the effective Fermi level, one can predict the appearance of the energy gap oscillations as a function of nanofilm thickness and almost five-fold enhancement of the energy gap for particular value of d . However, these predictions are significantly weakened if we increase the electron density up to the value measured for Al ($n_e = 1.8 \times 10^{23} \text{ cm}^{-3}$). In Fig. 4 we present the energy gap as a function of the nanofilm thickness and the electron density varying from 10^{21} cm^{-3} up to 10^{23} cm^{-3} . We restrict our analysis to the thickness range 1 – 3 nm for which the highest maxima of $\Delta(d)$ are observed in Fig. 1(a). Fig. 4 shows that the increase of the electron density results in the decrease of the period of $\Delta(d)$ oscillations. This behavior can be explained in terms of the quantization of the quasi-particle energy levels in the direction perpendicular to the plane. The energy level in the presence of the Cooper pairing can be well estimated by the single-electron energy level using the for-

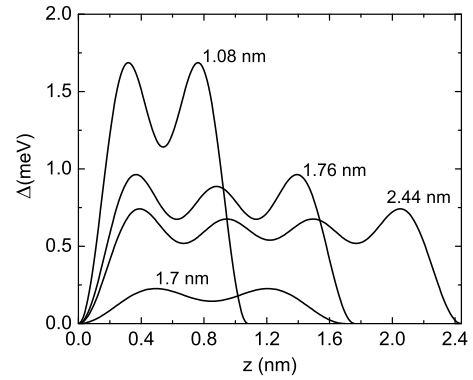


Figure 3 Position-dependent energy gap $\Delta(z)$ for nanofilm thicknesses marked by squares in Fig. 1(a).

mula $E \approx \hbar^2 \pi^2 \nu^2 / (2md^2)$, where the hard-wall potential is assumed in the z direction. It means that the quantum state ν passes through the Fermi level for the nanofilm thickness $d \approx \hbar \pi \nu / \sqrt{3\pi^2 n_e}$. The distance between two neighboring peaks can be estimated by $\Delta d = \pi / \sqrt{3\pi^2 n_e}$. In Fig. 4, the estimated nanofilm thicknesses for which the subsequent quantum states pass through the Fermi level are marked by white dashed lines. It can be seen that the single-electron energy level approximation can well reproduce the position of the energy gap peaks in the $\Delta(d, n_e)$ dependence.

The most important feature which can be found in Fig. 4 is the decrease of the amplitude of $\Delta(d)$ oscillations with increasing electron density. In Fig. 4 it is shown that if we increase the electron concentration, the maximum enhancement of the energy gap decreases from almost five-

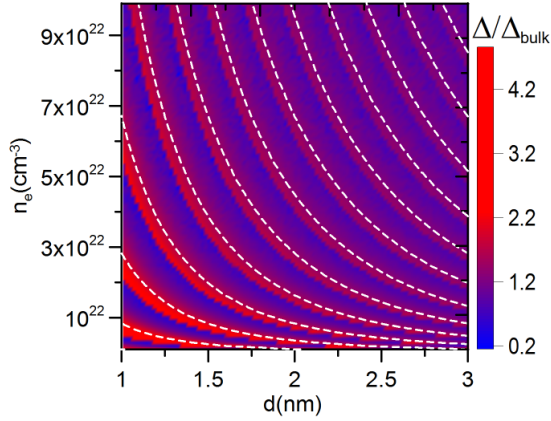


Figure 4 Superconducting energy gap Δ as a function of electron density n_e and nanofilm thickness d . White dashed lines mark the nanofilm thicknesses estimated from single-electron energy level, for which the subsequent quantum states pass through the Fermi level.

fold (as compared to Δ_{bulk}) for $n_e = 10^{21} \text{ cm}^{-3}$, to less than twice for the electron density $n_e = 10^{23} \text{ cm}^{-3}$. This fact allow us to conclude that the significant enhancement of the energy gap as a function of the nanofilm thickness can be observed only for the superconductor with the low concentration of carriers, e.g., SrTiO_3 which exhibits superconductivity in the carrier concentration regime $10^{18} - 10^{19} \text{ cm}^{-3}$ [27]. The fact that $\Delta(d)$ oscillations are less pronounced in the high-carrier concentration materials is crucial with respect to the experimental observation of the considered phenomena. In Fig. 5 we present $\Delta(d)$ calculated for the electron density $n_e = 1.8 \times 10^{23} \text{ cm}^{-3}$ corresponding to the bulk value for Al. This figure shows that for such high electron density the oscillations of the energy gap as a function of the nanofilm thickness are significantly suppressed as compared to the oscillations from the calculations with the effective Fermi level.

The microscopic model based on BdG equations allows to determine the parameters describing the superconducting state in metallic nanofilms when its thickness is reduced to few nanometers. However, in the nanoscale regime the superconductivity of the nanofilms is changed not only by the quantization of the quasi-particle energy, but also due to the fact that the phonon modes in the nanostructure (which mediate the Cooper pairing) strongly deviate from those observed in the bulk. Such deviation was experimentally reported for Ag nanofilm on the Fe substrate [28]. Therefore, the assumption that the electron-phonon coupling is constant and equal to the bulk value is the weak point of the presented considerations. The effect of confinement on the strength of the electron-phonon coupling as well as the electronic spectrum and its influ-

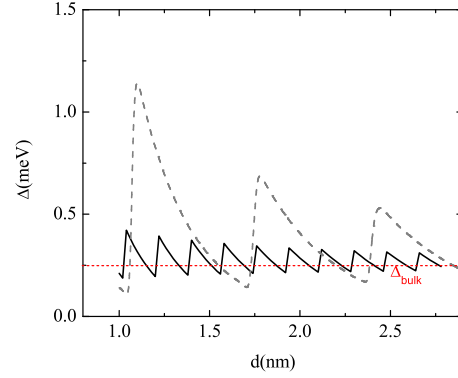


Figure 5 Superconducting energy gap Δ as a function of nanofilm thickness d calculated for electron density $n_e = 1.8 \times 10^{23} \text{ cm}^{-3}$ corresponding to the bulk value for Al. For comparison $\Delta(d)$ calculated for the effective Fermi level is displayed by the dashed gray line.

ence on the oscillations of the critical temperature has been recently investigated by Saniz et al. in Ref. [29]. Based on the Green function approach, the authors of Ref. [29] have derived the formula for the phonon-mediated attractive electron-electron interaction beyond the contact potential approximation presented in our paper. It has been found that the increase of density of states at the Fermi level suppress the critical temperature which is in contradiction to our and previous models. According to Ref. [29] the increase of the critical temperature observed for the superconducting nanofilms is due to the increase of the number of phonon modes what results in the enhancement of the electron-phonon coupling. Recently, the oscillatory behavior of the g coefficient as a function of the nanofilm thickness has been reported in Ref. [30]. Although the suppression of T_c with the increase of the density of states at the Fermi level [29] seems to be in agreement with the anticorrelation of T_c oscillations and the energy distribution of the quantum well states reported in Ref. [5], most of the papers [7] indicate the direct correlation between the T_c oscillations and the energy distribution of the quantum well states which confirms theoretical model presented in our paper. The presented discrepancy allow us to conclude that although it is well known that the T_c oscillations results from the changes in the electronic spectrum and the phonon modes induced by the quantum confinement, the microscopic mechanism governing this physical processes is still an open issue. Since in our opinion the calculation of the electron-phonon coupling in the ultra thin nanofilms requires *ab initio* methods, we treat $gN(0)$ and the Debye energy $\hbar\omega_D$ as parameters and calculate how the energy gap in the nanofilms changes as a function of these two quantities [Fig. 6(a) and Fig. 6(b)]. Fig. 6 shows that for each value of the nanofilm thickness the energy gap is

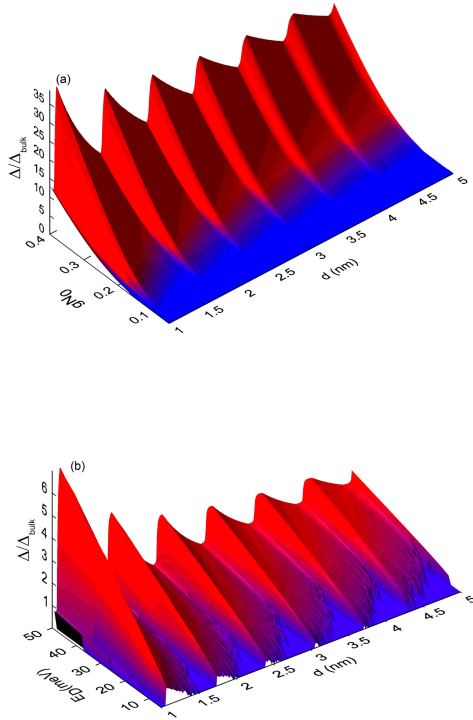


Figure 6 Thickness-dependent energy gap oscillations as a function of (a) the electron-phonon coupling $gN(0)$ and (b) the Debye energy $\hbar\omega_D$. Calculation carried out for the effective Fermi level $\mu_{bulk} = 0.9$ eV.

an increasing function of the parameters $gN(0)$ and $\hbar\omega_D$. Therefore, one can expect that the experimentally observed decrease of the electron-phonon coupling as a function of the nanofilm thickness results in the decrease of the amplitude of $\Delta(d)$ oscillations in the metallic nanofilm, which is the second factor in addition to the electron concentration which weakens the energy gap oscillations effect. It is also worth noting, that although the values of $\Delta(d)$ increase as a function of the parameters $gN(0)$ and $\hbar\omega_D$, the ratio between the maximum and the minimum value of the energy gap for each peak remains almost unaffected, e.g. it is about five for the first peak.

Comparison with experiment. The results presented in the paper show that the values of the electron density and the electron-phonon coupling are crucial parameters when it comes to the amplitude of the energy gap oscillations. Since both of these parameters strongly depend on the quality of the nanofilms which is directly related to the fabrication process, our results explain why the experimental data vary from one experiment to another. In this subsection we present direct comparison of the theoretical results with the experimental data on the energy gap for Al nanofilms [31]. Based on the measurements of small-area

aluminium superconductor-insulator-superconductor junction, the authors of Ref. [31] have determined the value of the energy gap for the film thicknesses $d = 5, 7, 10$ and 30 nm and found the enhancement of the energy gap with decreasing nanofilm thickness. It is worth mentioning that samples under consideration [31] had a granular structure with strong coupling between grains. It has been shown that the grain size does not have any appreciable effect on the value of the energy gap. This fact allows us to treat them as a sample as such with a high degree of crystallinity. In order to compare theoretical results with the experiment, we need to add to our model (limited to ideal case of uniform nanofilms) the effect coming from the surface roughness. It is well known that the films fabricated in experiments are not atomically uniform and only the average value of the thickness is known. In order to take into account such effect we adopt a simplified approach presented in Ref. [32], where the single electron energies in the presence of surface imperfection are approximated by

$$\xi_{k_x k_y \nu}^{surf} = \xi_{k_x k_y \nu} + \epsilon_{k_x k_y \nu} \left| \frac{\partial \xi_{k_x k_y \nu}}{\partial d} \right| \delta d \quad (8)$$

where $\xi_{k_x k_y \nu}$ is given by Eq.(6), $\epsilon_{k_x k_y \nu}$ is a random variable from the uniform distribution $[-1, 1]$ and δd is the variation of the nanofilm thickness related to the surface roughness.

Since the single electron energy depends on a random variable, the calculations of the superconducting energy gap for each nanofilm thickness has been repeated four thousand times assuming $\delta d = 1 \text{ ML} = 0.405 \text{ nm}$. This procedure allows us to obtain the range of the energy gap value related to the surface roughness for each nanofilm thickness. Fig. 7 presents the comparison of the theoretical results with the experimental data from Ref. [31]. The results presented in Fig. 7 has been calculated for the following values of parameters: $\mu_{bulk} = 0.95$ eV and $gN(0) = 0.175$. We see that the experimental data are well reproduced by the calculations with the surface roughness which are not taken into consideration in Ref. [33]. Our results not only explain the enhancement of the energy gap with decreasing the film thickness but also why the energy gap measured for the specified thickness differs significantly for different samples (see Fig. 7 or Ref. [31]).

4 Conclusions The influence of the electron density on the oscillations of the superconducting energy gap as a function of the nanofilm thickness is studied based on the self-consistent numerical solution of the Bogoliubov-de Gennes equations. We show, that in the ultra thin nanofilms, the strong enhancement of the superconducting energy gap for particular nanofilm thicknesses corresponds to the quasi-particle energy quantization induced by the confinement of electrons in the direction perpendicular to the film. In such situation, the Fermi sphere transforms into a series of parabolic subbands with energies that are decreasing with increasing nanofilms

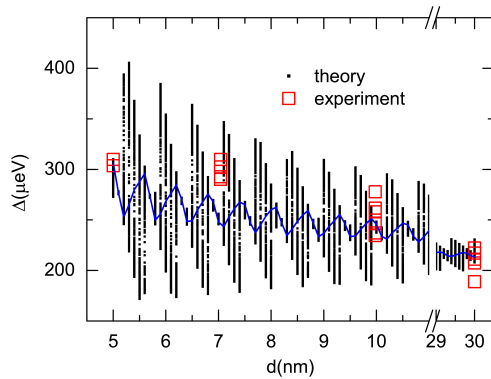


Figure 7 The thickness-dependent energy gap for Al nanofilms calculated with $\delta d = 1 \text{ ML} = 0.405 \text{ nm}$. Each of the black solid squares represents calculations for one of the 4000 random values of ϵ (Eq.8), red open squares are the experimental data from Ref. [31]. The blue line corresponds to superconducting gap averaged over the 4000 values obtained for every d .

thickness. Each time when the subband passes through the energy window $[\mu - \hbar\omega_D, \mu + \hbar\omega_D]$, the enhancement of the energy gap occurs in the $\Delta(d)$ dependence. In the present paper we study the influence of the electron density on the thickness-dependent energy gap oscillations in Al nanofilms. We find that the amplitude of the $\Delta(d)$ oscillations decreases with increasing electron density. The calculations carried out for the electron concentration corresponding to the one measured in the Al bulk show that $\Delta(d)$ oscillations are significantly reduced. This fact is relevant with respect to the experimental observation of the energy gap oscillations in the superconducting nanofilms. It allows us to restrict the experimental investigation to the low-carrier concentration superconductor e.g., SrTiO_3 . We also show that the period of $\Delta(d)$ oscillations is a decreasing function of the electron concentration. This behavior and the positions of the maxima in the $\Delta(d, n_e)$ dependence are well reproduced by the use of the single-electron energy level approximation. Since the reduction of the dimensionality changes considerably the phonon dispersion, we analyze the influence of the electron-phonon coupling and the Debye energy on the superconducting energy gap oscillations. These studies show that the decrease of the electron-phonon coupling observed experimentally in ultra thin nanofilm entails the decrease of the amplitude of $\Delta(d)$ oscillations. Although the presented calculations have been carried out for Al nanofilms, all conclusions regarding the influence of the electron density and the electron-phonon coupling on the energy gap oscillations remain also true for films made of other phonon-mediated superconductor. By appropriate choice of the considered parameters and including the effect of the surface roughness we compare our results with the experimental data.

Summing up, our results show that the changes in the electron density and the electron-phonon coupling constant have a strong influence on the magnitude of the considered phenomena and they should be taken into account in the theoretical investigations concerning superconductivity in metallic nanofilms. In particular, the increase of n_e and the decrease of g parameters leads to a relevant reduction of the oscillations amplitude, which could explain why in various experiments the considered phenomena hasn't been clearly visible. At the end, it is worth mentioning, that the matter of the nanofilm thickness dependance of the electron-phonon coupling constant is still not completely settled and with this respect, a proper *ab initio* calculations could make a substantial contribution in the complete theoretical description of the superconducting state in the nanofilm samples.

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