

Quantum-size effects on T_c in superconducting nanofilms

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Abstract. – An essential property of a high-quality metallic nanofilm is the quantization of the electron spectrum due to dimensional confinement in one direction. Quantum confinement has a substantial impact on the superconducting characteristics and leads to quantum-size variations of the critical temperature T_c with film thickness. We demonstrate that the Bogoliubov-de Gennes equations are able to describe the thickness-dependent T_c in nanofilms, and our results are in good agreement with recent experimental data on Pb flat terraces grown on silicon (*Science*, **306** (2004) 1915 and *Nature Phys.*, **2** (2006) 173). We predict that the quantum-size oscillations of T_c will be more pronounced for Al.

Recent advances in fabrication technology have fuelled a strong interest in the superconducting properties of nanoscale metallic low-dimensional structures. Systems which are a few nanometers in size, in one or more directions, exhibit quantum confinement which influences many physical effects and phenomena like, *e.g.* superconductivity. For films with thickness $d \leq l_e$ (mean free path) quantization of the electron motion in the direction normal to the film results in the formation of quantum-well states (QWS). Since the electron motion in the plane direction remains free, the band structure of the single-electron states is split into a series of two-dimensional (2D) subbands. Changing the film thickness gives rise to a modification of the energy ($\sim 1/d^2$) of the QWS. When a QWS passes through the Fermi surface, a new subband comes into play. For film thicknesses on the nanoscale, this passage is accompanied by a significant increase of the density of single-electron states at the Fermi level resulting in strong variations of the physical properties with changing film thickness.

Photo-electron spectroscopy has indeed demonstrated clear signatures of the formation of such QWS in thin metallic films (see, for instance, the papers [1, 2] about electronic properties of noble-metal layers). Moreover, recent experiments with Pb(111) nanofilms revealed that the surface energy [3] and the thermal stability [4] strongly varies with film thickness. These quantum-size variations were found to follow a damped oscillatory curve which could be described by a Friedel-like form [3, 4]. Very recently, quantum-size oscillations of the superconducting temperature T_c and perpendicular upper critical magnetic field $H_{c2\perp}$ were reported [5, 6] for Pb(111) flat terraces grown on silicon with atomic-scale uniformity in thickness (5–20 monolayers (ML)). These experiments represent an important advance over earlier

results on the thickness dependence of T_c in Sn [7] and Pb [8] thin films. For the first time a solid demonstration was given that the observed variations in T_c are correlated with the passages of QWS through the Fermi surface. In this letter we present the first quantitative description of the quantum-size effects on T_c in these Pb nanofilms. Our microscopic study is based on a numerical solution of the Bogoliubov-de Gennes equations [9], where the important QWS are included. Earlier works on this subject [10,11] were limited to a simplified multiband BCS model and did not investigate how the quantum-size variations of T_c are dependent on the relevant parameters.

A direct consequence of quantum confinement is a nonuniform spatial distribution of the superconducting order parameter $\Delta = \Delta(\mathbf{r})$. It is well known that the Bogoliubov-de Gennes (BdG) equations are a very powerful formalism which is able to describe a position-dependent order parameter [9]. In the absence of a magnetic field $\Delta(\mathbf{r})$ can be chosen as a real quantity, and the BdG equations read

$$\begin{pmatrix} H_e & \Delta(\mathbf{r}) \\ \Delta(\mathbf{r}) & -H_e \end{pmatrix} \begin{pmatrix} u_n(\mathbf{r}) \\ v_n(\mathbf{r}) \end{pmatrix} = E_n \begin{pmatrix} u_n(\mathbf{r}) \\ v_n(\mathbf{r}) \end{pmatrix}, \quad (1)$$

where the single-electron Hamiltonian is $H_e = -\frac{\hbar^2}{2m}\nabla^2 - \mu$ with μ the chemical potential. We investigate a clean nanosize specimen, and the periodic lattice potential is taken into consideration through the electron band mass m (set to the free electron mass here). The order parameter is related to the eigenfunctions $u_n(\mathbf{r})$ and $v_n(\mathbf{r})$ through the self-consistency relation $\Delta(\mathbf{r}) = g \sum_n u_n(\mathbf{r})v_n^*(\mathbf{r})(1 - 2f_n)$ with g the electron-phonon coupling and $f_n = f(E_n)$ the Fermi function. The summation range is over the eigenstates with $E_n > 0$ and $|\xi_n| < \hbar\omega_D$, where ω_D is the Debye frequency and $\xi_n = \int d^3r [u_n^*(\mathbf{r})H_e u_n(\mathbf{r}) + v_n^*(\mathbf{r})H_e v_n(\mathbf{r})]$ is the single-electron energy. The BdG equations are solved self-consistently for a given μ determined by the mean electron density $n_e = \frac{2}{V} \int d^3r \sum_n [|u_n(\mathbf{r})|^2 f_n + |v_n(\mathbf{r})|^2 (1 - f_n)]$ (here the sum is over all the states with $E_n > 0$), where $V = L_x L_y L_z$ is the system volume ($d = L_z \ll L_x = L_y$). In the case of strong deviations of the chemical potential from its bulk value (as is the case for thin films with thickness less than 1–2 nm), the iterative procedure should be repeated for various μ until the needed mean electron density is obtained. As the periodic boundary conditions are used for the x - and y -directions (in the plane of the film), we get $\Delta(\mathbf{r}) = \Delta(z)$ and, hence, (see eq. (1)),

$$u_n(\mathbf{r}) = \frac{e^{ik_x x}}{\sqrt{L_x}} \frac{e^{ik_y y}}{\sqrt{L_y}} u_{k_x, k_y, j}(z), \quad v_n(\mathbf{r}) = \frac{e^{ik_x x}}{\sqrt{L_x}} \frac{e^{ik_y y}}{\sqrt{L_y}} v_{k_x, k_y, j}(z), \quad (2)$$

where $n = \{k_x, k_y, j\}$ with k_x (k_y) the free electron wave vector in x (y)-direction and j the quantum number related to the electron motion in the z -direction normal to the film. Due to the electron confinement in the z -direction we have $u_{k_x, k_y, j}(0) = u_{k_x, k_y, j}(d) = 0$, $v_{k_x, k_y, j}(0) = v_{k_x, k_y, j}(d) = 0$. Thus, $u_{k_x, k_y, j}(z)$ and $v_{k_x, k_y, j}(z)$ can be expanded in terms of the states

$$\varphi_l(z) = \sqrt{\frac{2}{d}} \sin \left[\frac{\pi(l+1)z}{d} \right] \quad (3)$$

with $l = 0, 1, 2, \dots$. A detailed description of our theoretical approach will be published elsewhere [12].

In fig. 1 we show numerical results for the superconducting temperature T_c and the density of single-electron states at the Fermi level (per spin projection and unit volume) as functions of the film thickness for Al and Pb (in the calculations we kept $L_x = L_y > 500$ nm such

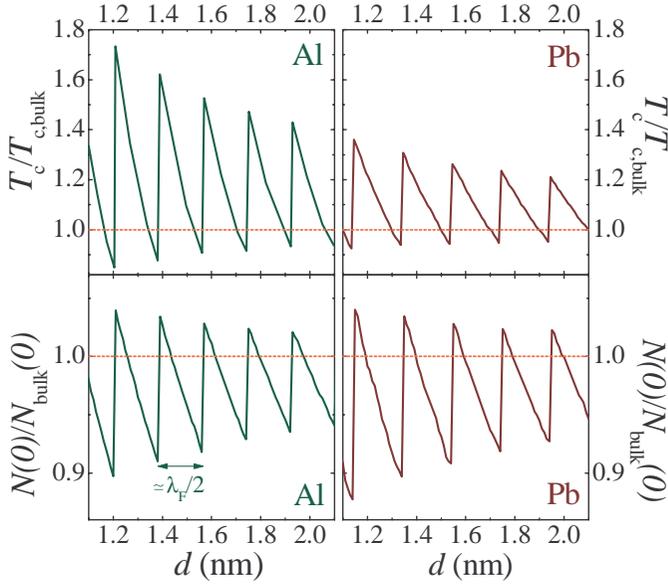


Fig. 1 – The critical temperature T_c (the upper panels) in units of the bulk superconducting temperature $T_{c,\text{bulk}}$ and the relative density of single-electron states at the Fermi level per unit volume and per spin projection (the lower panels).

that the results are valid in the limit $L_x, L_y \rightarrow +\infty$). For Pb (Al) we used the following parameters: $\hbar\omega_D/k_B = 96$ (375) K, $gN_{\text{bulk}}(0) = 0.39$ (0.18) and $\mu_{\text{bulk}} = 9.47$ (11.7) eV as given in standard textbooks [9,13,14]. Here k_B is the Boltzmann constant, $N_{\text{bulk}}(0) = mk_F/(2\pi^2\hbar^2)$ denotes the bulk density of single-electron states per unit volume per spin projection and k_F is the 3D Fermi wave number. Temperature dependence of the chemical potential is negligible for $T < T_c$, and, hence, we can write $k_F = \sqrt{2m\mu_{\text{bulk}}}/\hbar$. As one can see from fig. 1 (the upper panels), a sawtooth behavior for T_c is obtained. This result is more complicated than the simple Friedel-like expression $\sim \cos(2k_F d)/d^\gamma$ ($\gamma \approx 1$) typical for the surface energy and thermal stability function [3,4].

The physics of the above superconducting oscillations can be sketched as follows. Since the classical papers by Gor'kov [15] and Bogoliubov [16], it is known that the superconducting order parameter $\Delta(\mathbf{r})$ can be interpreted as the wave function describing the center-of-mass motion of a Cooper pair. The Cooper pairs are influenced by the surrounding electrons of the Fermi sea so that the single-fermion states with energies well below the Fermi level do not make any essential contribution to the Cooper-pair wave function and, hence, to the superconducting order parameter [17]. As a result, the order parameter (and T_c) will be dependent on the density of the single-electron states situated in the nearest vicinity of the Fermi level. Quantization of the electron motion in the direction normal to the film leads to the formation of QWS and results in a splitting of the band of single-electron states in a series of subbands. When the bottom of a given subband passes through the Fermi surface when changing film thickness, the density of states increases abruptly (see the lower panels of fig. 1). For nanofilms, this increase is significant. However, when approaching the bulk regime, the effect is washed out. Thus, the density of single-electron states per unit volume and per spin projection shows remarkable sawtooth damped oscillations which are smoothed for films with thickness fluctuations. The same occurs for the order parameter (spatially

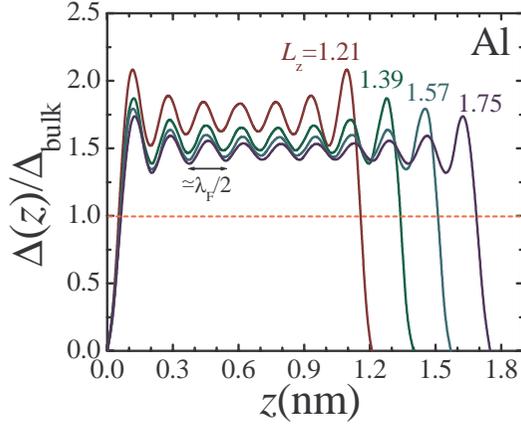


Fig. 2 – The spatial distribution of the superconducting order parameter in an Al nanofilm at resonant thicknesses $d = 1.21, 1.39, 1.57$ and 1.75 nm.

averaged) and T_c . The single-electron states located at the bottom of a subband give almost the same contributions to the superconducting properties. This plays the role of amplifier: an increase of T_c is more pronounced than a corresponding increase in the density of states. The “amplification” factors are about 6 for aluminum and 3 for lead. We remark that, in contrast to the naive expectation that T_c should be equal to its bulk value when $N(0) = N_{\text{bulk}}(0)$, we find $T_c > T_{c,\text{bulk}}$ for such cases. Thus, following Blatt and Thompson [10], the enhancement of superconductivity due to the passage of a QWS through the Fermi surface can be called a *shape superconducting resonance*.

Magnitudes of the shape resonances in $T_c/T_{c,\text{bulk}}$ are very sensitive to the governing parameters ω_D , g and μ_{bulk} (the chemical potential μ appearing in the BdG equations depends on the mean electron density and, so, is fully determined by μ_{bulk}). Results of a numerical solution of the BdG equations plotted in fig. 1 show that oscillations of $T_c/T_{c,\text{bulk}}$ are becoming less profound with increase of any of these parameters. The point is that such increase leads to an increase of the “condensation” energy of the superconducting electrons. So, in order to produce the same deviations from the bulk value some additional confinement energy is required. Therefore a systematic shift of the shape superconducting resonances to smaller film thicknesses is observed (compare Pb results with those of Al in fig. 1).

The distance between two neighboring superconducting shape resonances is about π/k_F , which is one-half of the 3D Fermi wavelength λ_F (see fig. 1). Because the single-electron energies are much larger than the energy for Cooper pairing, the period of QWS passages through the Fermi surface can be explained in terms of the states given by eq. (3). The energy of the l -state is $\hbar^2\pi^2(l+1)^2/(2md^2)$ and, so, this state passes through the Fermi surface for film thickness $\hbar\pi(l+1)/\sqrt{2m\mu}$. Then, the distance between two neighboring resonances can be estimated as $\hbar\pi/\sqrt{2m\mu}$. Though μ increases with decreasing film thickness, this increase is not very significant for $d > 1$ nm. Thus, using $\mu \approx \mu_{\text{bulk}}$, we get $\lambda_F/2$ for the QWS-period in agreement with the numerical results presented in fig. 1.

The spatial distribution of the superconducting condensate is strongly nonuniform in the presence of quantum confinement. In fig. 2 the superconducting order parameter $\Delta(z)$ is plotted as a function of the coordinate normal to the film for a sequence of resonance points. As seen, $\Delta(z)$ shows profound oscillations with the period about $\lambda_F/2$. Notice that $\Delta(z) = 0$ at the edge of the film while in the Ginzburg-Landau theory this is not the case [18].

Using the standard Fermi level for Pb, $\mu_{\text{bulk}} = 9.47 \text{ eV}$, one expects that in Pb(111) nanofilms QWS cross the Fermi surface with a period less than 1 ML (for Pb(111) films 1 ML corresponds to 0.286 nm [19]). However, photo-electron spectroscopy demonstrates that this period is larger and close to 2 ML [5]. It is worth noting that photoemission experiments on thin films made of Cu, Ag, Au, Co and Fe revealed the same disagreements [1, 2]. The general explanation is that the above discrepancy is an artifact of incorporating the periodic lattice potential in terms of the band mass [1, 2]. Indeed, first-principle calculations of the quantized band structure of Pb(111) films have shown that the period in question is about 2.2 ML [19]. This is in good agreement with the experimental observation $\approx 2 \text{ ML}$ [5]. In order to remedy this we introduce an effective Fermi level $\mu_{\text{bulk}} = 1.25 \text{ eV}$ (the same can be done by effective reduction of the band mass) and solve the BdG equations within the single-parabolic band approximation (*i.e.*, eq. (1)). Note that the introduction of the effective Fermi level corresponds to a change of the reference point of the Pb band structure as suggested in ref. [19].

In order to observe experimentally clear signatures of the QWS-formation, ultrathin crystalline films with atomic-scale uniformity in thickness are needed. In this case film thickness is an integer number of monolayers N ($N = d/a$, where the lattice spacing $a = 0.286 \text{ nm}$ [19] for Pb(111) films). As mentioned above, in Pb(111) films the periodicity of the Fermi surface QWS-crossing is about 2 ML, which results in oscillations [3–6] of the physical properties between films with even and odd number of monolayers (the even-odd oscillations). A direct consequence of these oscillations is a preference of even or odd number of monolayers for the occurrence of stable ultrathin films [5]. In experiments Pb films were grown on a Si(111) substrate [3–6, 20] and protected with an Au [5, 6] or Ge [20] cover layers. Such substrate and protecting coverage were shown to change the electron-phonon coupling in ultrathin films (with respect to bulk) due to an interface effect [21]. For instance, in ultrathin films ($N < 12\text{--}16 \text{ ML}$) of Ag on Fe(100) and V(100) substrates the electron-phonon coupling was found to be significantly larger than in bulk and decreases down to the bulk value as the film thickness increases [21, 22]. Deviations of the coupling constant from its bulk limit follow approximately an overall $1/N$ -dependence [21] and exhibit damped oscillations with film thickness [21, 22]. This $1/N$ -dependence can be understood (see [23]) as due to the fact that the relative number of film atoms at the interface is proportional to $1/N$. Measurements

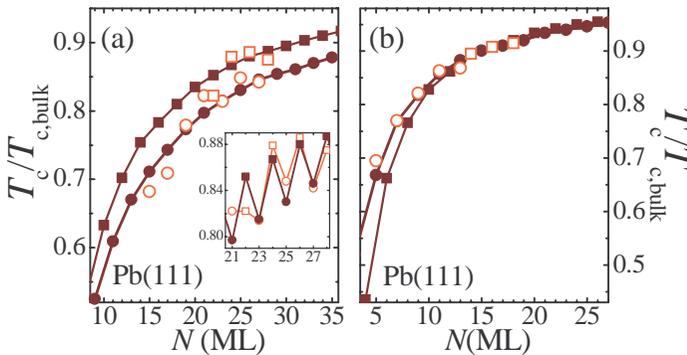


Fig. 3 – The superconducting temperature for the odd-layered (circles) and even-layered (squares) Pb(111) nanofilms grown on silicon: (a) the experimental data from ref. [5] (empty symbols) and our theoretical results (filled symbols) for $g_1(\pi)N_{\text{bulk}}(0) = 0.204$ and $g_1(2\pi)N_{\text{bulk}}(0) = 0.26$ (inset highlights the even-odd oscillations); (b) the experimental data from ref. [20] (empty symbols) and our results (filled symbols) calculated for $g_1(\pi)N_{\text{bulk}}(0) = 0.077$ and $g_1(2\pi)N_{\text{bulk}}(0) = 0.177$.

of the Eliashberg λ -factor in Pb(111) ultrathin flat terraces [5] on silicon showed that in this case the electron-phonon coupling is lower than in bulk and gradually increases towards the bulk value as the film gets thicker. Oscillations of the coupling constant with film thickness are clearly visible here, as well [5]. Keeping in mind these results, we can expect that for the experimentally interesting case of a Pb(111) film grown on a silicon substrate the dependence of the electron-phonon coupling constant on film thickness can be approximated by

$$g = g_0 - \frac{g_1(2k_FaN)}{N}, \quad (4)$$

where $g_0N_{\text{bulk}}(0) = 0.39$ (this provides the correct bulk limit) and $g_1(x)$ is a function oscillating with the period 2π . The variations of the electron-phonon coupling constant with film thickness appear due to changes in the density of states at the Fermi level [21]. Therefore the distance between two neighboring superconducting resonances π/k_F determines the oscillating period for $g_1(2k_FaN)$. For Pb(111) films $\pi/k_F \approx 2a$, then we have $g_1(2k_FaN) \approx g_1(\pi)$ for the odd-layered films and $g_1(2k_FaN) \approx g_1(2\pi)$ for the even-layered films. So, instead of operating with an unknown function g_1 we need only two parameters: one for the even-layered films, another for the odd-layered films.

The experimental results of ref. [5] (empty circles for the odd-layered films and empty squares for the even-layered films in fig. 3(a)) are in good agreement with our theoretical predictions if we take $g_1(\pi)N_{\text{bulk}}(0) = 0.204$ and $g_1(2\pi)N_{\text{bulk}}(0) = 0.26$. Theoretical results for the odd-layered (even-layered) films are filled circles (squares) here. Inset in fig. 3(a) demonstrates that not only experimental trends for odd- and even-layered Pb(111) nanofilms but also a very fine structure of the even-odd oscillations in T_c are well reproduced. Note that the superconducting temperature in Pb(111) terraces grown on silicon with a protecting Au layer (see ref. [5] and fig. 3(a)) is different from T_c found in Pb(111) terraces with an amorphous Ge protecting cover (see ref. [20]). In fig. 3(b) we demonstrate that our theoretical data (the solid circles and squares for the odd- and even-layered samples, respectively) agree with the experimental results of ref. [20] (the empty circles and squares, respectively) when $g_1(\pi)N_{\text{bulk}}(0) = 0.077$ and $g_1(2\pi)N_{\text{bulk}}(0) = 0.177$. There is no available data on the even-odd oscillations in the latter case.

In conclusion, quantum-size effects on the superconducting temperature in nanofilms were investigated by a numerical self-consistent solution of the Bogoliubov-de Gennes equations. We presented the first quantitative description of recent experimental data for the film thickness dependence of T_c in Pb(111) flat terraces grown on silicon with atomical-scale uniformity in thickness.

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