Quantum size effects in Friedel oscillations inside films

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ABSTRACT

An analytical formula of density oscillations is found for metallic films of finite thickness. The result shows that the quantum size effect on density oscillations is surprisingly more evident in the middle of the film. As a result, the density oscillations in a finite film cannot be regarded as a simple addition of the two sets of Friedel oscillations for half-infinite metal no matter how thick the film is. This analytical result is confirmed by our numerical jellium-model computation. Such quantum size effect should exist in all the electron-mediated interactions that are driven by the Friedel oscillations. As an example, we indeed find it also exists in Ruderman–Kittel–Kasuya–Yosida interactions inside films.

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1. Introduction

Friedel oscillations are electron density waves induced by impurities or step edges[1]. Due to their fundamental importance, the Friedel oscillations have been widely studied in many different systems. They were observed directly in experiment with scanning tunneling microscopy (STM) [2–7], and recently, Friedel oscillation has been used to see the Fermi surface in real space [8]. Friedel oscillations have also been studied in metallic films, in particular, there appear indications that Friedel oscillations may be responsible for the robust quantum size effects observed in Pb (111) films [9].

Motivated by this development, we conducted a careful examination of the density oscillations in metallic films. For a half-infinite metallic film, the deviation of the electron density from the averaged value (Friedel oscillations) has the following form [10]:

$$\delta n(x) \sim \frac{\cos 2(k_{\mathrm{f}} x)}{x^2}, \tag{1}$$

where k_{f} is the Fermi wavevector and x is the distance from the surface. As one may expect, for a not-so-thin metallic film, its density oscillation should be a simple addition of two sets of the Friedel oscillations in Eq. (1) that originate from the two surfaces. We find an analytical formula for the density oscillations in a finite metallic film. This analytical formula has two important features: (1) it cannot be regarded as a simple addition of two sets of Friedel oscillations in Eq. (1); (2) it shows that the quantum size effect on density

oscillation is surprisingly more evident in the middle of the film. This analytical result is confirmed by our numerical computation with jellium model.

This strong finite size effect in the middle of the film can be attributed to the discretization of energy bands induced by the confinement of two surfaces. In obtaining Eq. (1), one needs to replace a summation over discretized wavevector k with an integration [10]. However, in the middle of the film, one always has $x \sim L/2$ (L is the thickness of the film) and consequently $x\delta k \sim \pi$ ($\delta k \sim 2\pi/L$) no matter how thick the film is. This finite $x\delta k$ prevents replacing the summation with integration.

It should be noted here that such quantum size effect should universally exist in all the electron-mediated interactions that are driven by the Friedel oscillations[11–19]. Therefore, our results will have wide applications in nano-materials. As an example, we have investigated the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction inside films, which is regarded as one of the fundamental interactions in magnetic multilayer system [15–17]. We find that quantum finite size effect cannot be ignored when the distance between two magnetic moments is bigger than 0.2L (L is the total film thickness).

2. Quantum size effect in Friedel oscillations

Consider a free-standing metallic film of thickness L (Fig. 1). For simplicity, we ignore the ionic lattice and the Coulomb interactions and treat the film as a collection of free electrons confined between two potential barriers at the surfaces. In this case, the wave functions for electrons can be written as

$$\psi_{k_n,k_y,k_z} = \psi_{k_n}(x) \exp\left[i\left(k_y y + k_z z\right)\right], \tag{2}$$

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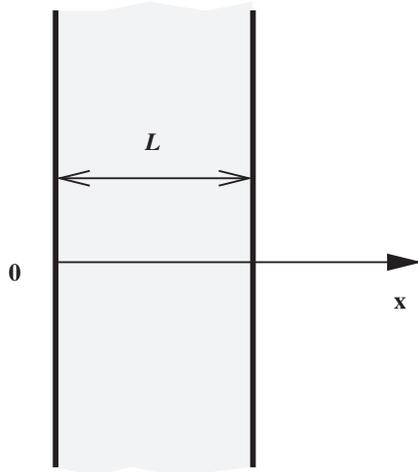
Fig. 1. A metallic film of thickness L.

where k_n is the wave vector along the x direction and it is discretized due to the confinement by the two surfaces. The corresponding energy up to a trivial constant is

$$E\left(k_n, k_y, k_z\right) = \frac{1}{2}\left(k_n^2 + k_y^2 + k_z^2\right). \tag{3}$$

When the two surfaces are regarded as two impenetrable walls, we have $\psi_{k_n}(x) = \sqrt{\frac{2}{L}} \sin(n\pi x / L)$[20,21]. This implies that in the region far away from the film surfaces we should have

$$\psi_{k_n}(x) = \sqrt{\frac{2}{L}} \sin\left[k_n x - \gamma(k_n)\right] \tag{4}$$

with

$$k_n = \frac{n\pi}{\mathcal{L}}, \qquad \mathcal{L} = L + 2\delta, \tag{5}$$

The parameter $\delta(\ll L)$ is to be determined, $\gamma(k_n)$ is an additional phase shift in the wave function when considering the factor that electrons can penetrate into the vacuum. Generally, the amplitude is a function of wave vector k_n, and should be expressed as $\sqrt{2 / (L + l_n)}$, where $l_n \sim O(1)$ is a function of k_n. In Appendix A, we find that replacing $\sqrt{2 / L}$ with $\sqrt{2 / (L + l_n)}$ just adds $O(1/L^3)$ terms in the electron density, so we can ignore it.

As a result, the electron density in the region far away from the film surface has the following form:

$$n(x) = \frac{1}{\pi L} \sum_{n=1}^{N} \left(k_f^2 - k_n^2\right) \sin^2\left[k_n x - \gamma(k_n)\right], \tag{6}$$

where N is the total number of occupied subbands. The Fermi wave vector k_f can be expressed as

$$k_f = \frac{\pi}{\mathcal{L}}(N + \beta), \ \beta \in (0, 1). \tag{7}$$

Note that the system has a symmetry that

$$\psi_{k_n}^2(x) = \psi_{k_n}^2(L - x), \tag{8}$$

this symmetry leads to

$$\gamma(k_n) = \frac{n\pi L}{2L} - \frac{\pi}{2} m_1 = -k_n\delta - \frac{\pi}{2} m_2, \tag{9}$$

where both m_1 and m_2 are integers. It is reasonable to assume that the phase shift γ is a continuous function of k and $\gamma(0) = 0$. This means that we have $m_2 = 0$ and $\gamma(k) = -k\delta$. Regarding δ as a constant, with the phase rule [22]

$$\frac{2}{k_f^2} \int_0^{k_f} k\gamma(k)\mathrm{d}k = -\frac{\pi}{4}, \tag{10}$$

we have $\delta = (3/8)(2\pi/3)^{2/3} r_s$. This recovers the results by Schulte [23] and Stratton [24]. Generally, δ is not a constant and in this paper we treat it as a function of n/N (Eq. (A.1) in Appendix A). With the above results, we can now sum out the electron density in Eq. (6) and arrive at (see Appendix A for derivation details)

$$n(x) = n_0 \left\{ 1 + \frac{3(1-\beta)\eta^2(x)\cos2[(k_f - \beta k_1)x - \gamma_f]}{(2k_f x)^2} \right. $$
$$\left. + \frac{3\beta\eta^2(x)\cos2[(k_f + (1-\beta)k_1)x - \gamma_f]}{(2k_f x)^2} \right\}, \tag{11}$$

where $\eta(x) = \left(\frac{\pi x}{L}\right) / \sin\left(\frac{\pi x}{L}\right)$ and $k_1 = \pi/L$.

At the limit $x/L \to 0$, we can replace $\sin \pi x/L$ with $\pi x/L$, and obtain

$$n(x) = n_0 \left[1 + \frac{3\xi \cos2(k_f x - \gamma_f)}{(2k_f x)^2} \right] (\xi = 1), \tag{12}$$

which recovers the Friedel oscillations of electron density in a half infinite metal [10]. This is no surprise: in a half infinite metal, we have $L \to \infty$ so that the limit $x/L \to 0$ is always satisfied. In contrast, for a film of finite thickness, we always have $x/L \sim 1/2$ near the middle of the film. In other words, we cannot reach the limit $x/L \to 0$ in the central region of the film no matter how thick the film is. Note that the use of ξ in Eq. (12) is for the convenience of future discussion.

The analytical formula in Eq. (11) is the central result of this work. A careful examination of the equation offers an insight into the physics behind the analytical form. We first notice that there are two wave vectors in Eq. (11), one is $2(k_f - \beta k_1)$ and the other is $2[k_f + (1-\beta)k_1]$. The difference between them is $k_1 = \pi/L$, which is small for a thick film ($L \gg 1$). However, when x is comparable to L such as in the central region of the film, the phase shift caused by the difference k_1 is not small at all. Therefore, we have to retain k_1. In contrast, when x/L is small, we can ignore k_1. Since we have $\eta(x) \sim 1$ at the same time, Eq. (11) is reduced to the well-known result in Eq. (12).

The above analysis also indicates that the electron density in Eq. (11) is the result of the surface confinement because the difference k_1 is caused by the discretization of electron energy bands. At places where x is small compared to the film thickness L, the system does not feel much of the discretization and one can replace the summation in Eq. (6) with integration and obtain Eq. (12). However, when x is comparable to L, the discretization is always felt by the system and one can not replace the summation with integration.

We have shown and explained that the electron density in the central region of the film is different from a well-known result. However, one may still wonder whether the electron density in a film can be regarded as a simple superposition of two sets of Friedel oscillations for a half-infinite metal. In other words, the question is whether $n(x)$ in Eq. (11) is approximately equal to

$$n^s(x) = n_0 \left\{ 1 + \frac{3\cos2(k_f x - \gamma_f)}{(2k_f x)^2} + \frac{3\cos2[k_f(L - x) - \gamma_f]}{[2k_f(L - x)]^2} \right\}. \tag{13}$$

To answer this question, we focus on a small interval near the middle of the film. In such an interval, the electron density should take

the form of $A\cos(k_F x + \Theta)$. Straightforward computation shows the amplitude A obtained from Eq. (11) is

$$A_1 = \frac{3n_0\eta^2(x_\alpha)}{(2k_F x_\alpha)^2} \sqrt{(2\beta-1)^2\sin^2\phi_\alpha + \cos^2\phi_\alpha}, \tag{14}$$

where x_α is the central point of the interval and $\phi_\alpha = \frac{\pi}{L}x_\alpha$. The amplitude from Eq. (13) is

$$A_2 = \frac{3n_0}{(2k_F x_\alpha)^2} \sqrt{\xi^2(x_\alpha) + 2\xi(x_\alpha)\cos(2\beta\pi) + 1}, \tag{15}$$

where $\xi(x_\alpha) = [x_\alpha/(L-x_\alpha)]^2$. The deviation of the ratio between the two amplitudes from one is

$$\Delta A(x_\alpha,\beta) = \frac{A_1}{A_2} - 1 = \eta^2(x_\alpha)\sqrt{\frac{(2\beta-1)^2\sin^2\phi_\alpha + \cos^2\phi_\alpha}{\xi^2(x_\alpha) + 2\xi(x_\alpha)\cos(2\beta\pi) + 1}} - 1. \tag{16}$$

This deviation measures the difference between the true electron density in Eq. (11) and the density resulted from the simple superposition as given in Eq. (13). Since β is a function of the film thickness L, ΔA is also a function of x_α and L.

We have plotted ΔA of four situations that $x_\alpha = 0, L/10, 2L/5, L/2$ in Fig. 2. It is evident from the figure that ΔA is zero at only a couple of isolated values of β. The figure also shows that $\Delta A > 0$ when $\beta < \beta_0$ or $\beta > 1 - \beta_0$ and $\Delta A < 0$ when $\beta_0 < \beta < 1 - \beta_0$. Our numerical results show that the variation of β_0 is very small (from 0.18 for $x_\alpha/L \to 0$ to 0.13 for $x_\alpha/L = 1/2$). This means that we can regard ΔA not changing its sign for all x_α. Since β is a function of the film thickness L, the results shown in Fig. 2 conclude that the electron density in a metallic film cannot be regarded as the simple superposition of two sets of Friedel oscillations in half infinite metal. As indicated in the figure, the Friedel oscillations are enhanced up to about 23%.

We now calculate the electron density using the density functional theory (DFT) for a comparison with the analytic form in Eq. (11). To overcome the instability caused by the long range of the Coulomb interaction between electrons, we apply the method used by Monnier and Perdew [25], which was originally proposed in Ref. [26].

Our numerical results for Pb film ($L = 60d_0, \beta = 0.17$) are plotted in Fig. 3 and are compared to our analytical result Eq. (11). It is clear that the two curves match each other quite well when x is larger than $10d_0$. This implies that our analytical results are even valid when the Coulomb interaction and correlation effects are taken into account. Note that the parameter β can be obtained from our numerical results.

It should be emphasized here that it is reasonable that our analytical result Eq. (11) with free electron model agrees well with

the numerical results, where the influence of the interaction between electrons is taken into account. This was addressed in Ref. [10]. In a half infinite metal, free electron model gives a density expressed by Eq. (12) with $\xi = 1$ (sine-wave form of wave function is used in calculating Eq. (12)). When the influence of interactions is considered, one can substitute the sine-wave form of wave into the self-consistent Kohn–Sham equation, and get the wave function that have taken into account the influence of the Coulomb interactions, exchange and correlation effects. It was found that the parameter ξ increases from 1.004 at $r_s = 2$ to 1.07 at $r_s = 6$ [10]. This implies that free electron model is sufficient in calculating Friedel oscillations.

Although we need $L \gg 1$ in our derivation, we find that a significant portion of the film around the middle of the film can be well described by Eq. (11) even when the film is quite thin. For example, as shown in Fig. 4, the numerical results for Pb ($L = 11d_0$, $\beta = 0.74$) can be fitted very well with our theoretical expression. Note that one may find Eq. (11) does not have space inversion symmetry for a small L because we have omitted some high order terms in the cosine functions, in fact we should use Eq. (A.7) for the symmetry requirement when the film is not very thick.

Note that our analytical result is effective in most of the region inside the film except the areas near the two surfaces when the film thickness is large enough. So, it is a supplementary result to the work of Takahashi and Onzawa [27], in which, the electron density near the

Fig. 3. Numerical results of the ratio n/n_0 for Pb film of thickness $L = 60d_0$ in comparison with the analytical results.

Fig. 2. The deviation ΔA as a function of β for different values of $x_\alpha = 0, L/10, 2L/5, L/2$.
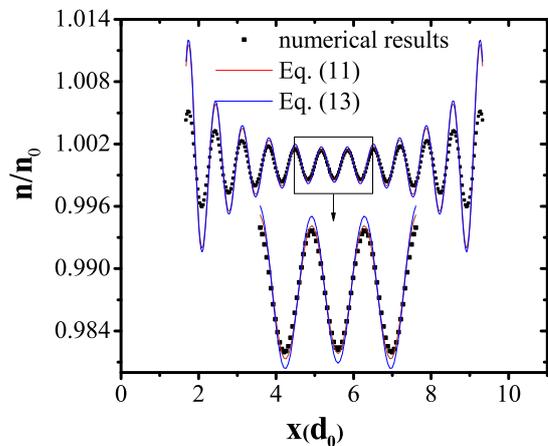
Fig. 4. Numerical results of the ratio n/n_0 for Pb film of thickness $L = 11d_0$ in comparison with the analytical results.

metal surface obtained from a "shifted" step potential was shown to agree well with the jellium calculations.

3. Quantum size effect in RKKY interaction

We find that such effect also exists in RKKY interactions inside films. An analytical formula, different from the traditional one, is obtained for the indirect exchange coupling between two localized magnetic moments in a finite film. In this paper, we focus on the quantum size effect in RKKY interaction and ignore the topological property of Fermi surface [17]. According to the works of Ruderman, Kittel [28], Kasuya [29], and Yosida [30], the RKKY interaction between two localized magnetic moments can be expressed as [31]

$$\mathcal{H}_{\text{RKKY}} = \hat{\mathbf{I}}_{\mathbf{n}} \cdot \hat{\mathbf{I}}_{\mathbf{m}} \mathcal{J}(|\mathbf{R}_n - \mathbf{R}_m|), \tag{17}$$

and

$$\mathcal{J}(|\mathbf{R}|) = \frac{4J^2 m^* k_f^4}{(2\pi)^3 \hbar^2} \left\{ \frac{\cos 2k_f R}{(2k_f R)^3} - \frac{\sin 2k_f R}{(2k_f R)^4} \right\}. \tag{18}$$

Where $\hat{\mathbf{I}}_{\mathbf{n}}$ are the localized moments, J is the exchange coupling constant, E_f is the Fermi energy, and k_f is the Fermi wave vector.

In the case of film, for simplicity, we impose the periodic boundary condition and compute $\mathcal{J}^f(\mathbf{R}) + \mathcal{J}^f(\mathbf{R} - L\hat{x})$ (the superscript f denotes film) by changing the integration of q_x in Eq. (13) of Ref. [32] to summation

$$\mathcal{J}^f(\mathbf{R}) + \mathcal{J}^f(\mathbf{R} - L\hat{x}) = -\frac{m^* J^2}{(2\pi)^5 \hbar^2} \iint \sum_{q_x} \cos \mathbf{q} \cdot \mathbf{R} F(q) \Delta q_x dq_y dq_z, \tag{19}$$

where $F(q)$ is (Eq. (15) in Ref. [32])

$$F(q) = \frac{1}{2}k_f + \frac{1}{2q}\left(k_f^2 - \frac{1}{4}q^2\right) \ln\left|\frac{q + 2k_f}{q - 2k_f}\right|. \tag{20}$$

To further simplify the matter, we assume that the two magnetic impurities have the same y, z coordinates. In this case, we can use polar coordinates with $\mathbf{R}$ parallel to the x axis (perpendicular to the film surfaces). After integration over ϕ, Eq. (19) becomes

$$J^f(R) + J^f(L - R) = -\frac{m^* J^2}{(2\pi)^4 \hbar^2} \int_0^\infty F(q)q^2 \sum_\theta \cos(qR\cos\theta) \sin\theta \Delta\theta dq$$
$$= \frac{m^* J^2}{(2\pi)^4 \hbar^2} R^{-1} i^{-1} \eta(R) \int_{-\infty}^\infty e^{iqR - iI(q)R} F(q) q dq, \tag{21}$$

where

$$I(q) = q - \left[\frac{qL}{2\pi}\right] \frac{2\pi}{L} - \frac{\pi}{L}, \tag{22}$$

$$\eta(R) = \frac{\frac{R}{L}\pi}{\sin\frac{R}{L}\pi}, \tag{23}$$

the square bracket denotes round-down to the closest integer. Finally, we obtain

$$\mathcal{J}^f(R) + \mathcal{J}^f(L - R) = \frac{4J^2 m^* k_f^4}{(2\pi)^3 \hbar^2} \left\{ \frac{B^f(R)\cos\left(2k_f R + \Phi_1^f(R)\right)}{(2k_f R)^3} \right.$$
$$\left. - \frac{C^f(R)\sin\left(2k_f R + \Phi_2^f(R)\right)}{(2k_f R)^4} \right\}, \tag{24}$$

where

$$B^f(R) = \eta(R)^3 \sqrt{4\beta^2(\beta-1)^2 \sin^4\frac{\pi R}{L} + \cos^2\frac{\pi R}{L}}, \tag{25}$$

$$C^f(R) = \eta(R)^4 \left\{ \left[1 - 2\left(\beta^2 + \frac{1}{3}\right)\sin^2\frac{\pi R}{L} + \frac{4}{3}\beta^3 \sin^4\frac{\pi R}{L}\right]^2 \right.$$
$$\left. + \beta^2 \sin^2\frac{2\pi R}{L}\left(1 - \frac{2\beta^2}{3}\sin^2\frac{\pi R}{L}\right)^2 \right\}^{\frac{1}{2}}, \tag{26}$$

$$\beta = \frac{k_f L}{2\pi} - \left[\frac{k_f L}{2\pi}\right], \tag{27}$$

and

$$\Phi_1^f(R) = \arctan\frac{2\beta\left(1 - \beta\sin^2\frac{\pi R}{L}\right)\tan\frac{\pi R}{L}}{1 - 2\beta^2 \sin^2\frac{\pi R}{L}} - \frac{2\beta\pi R}{L}(+\pi), \tag{28}$$

$$\Phi_2^f(R) = \arctan\frac{\beta\sin\frac{2\pi R}{L}\left(1 - \frac{2\beta^2}{3}\sin^2\frac{\pi R}{L}\right)}{1 - 2\left(\beta^2 + \frac{1}{3}\right)\sin^2\frac{\pi R}{L} + \frac{4}{3}\beta^3\sin^4\frac{\pi R}{L}} - \frac{2\beta\pi R}{L}(+\pi). \tag{29}$$

In $\Phi_1^f(R)$, $+\pi$ means that we need to add π when $\cos\frac{\pi R}{L}(1 - 2\beta^2 \sin^2\frac{\pi R}{L}) < 0$; similarly for $\Phi_2^f(R)$, $+\pi$ means that we need to add π when $1 - 2\left(\beta^2 + \frac{1}{3}\right)\sin^2\frac{\pi R}{L} + \frac{4}{3}\beta^3\sin^4\frac{\pi R}{L} < 0$.

Now we can consider the influence of such effect in RKKY interaction by comparing $\mathcal{J}^f(R) + \mathcal{J}^f(L-R)$ with $\mathcal{J}(R) + \mathcal{J}(L-R)$. From Eq. (18), we can find that the expression of $\mathcal{J}(R) + \mathcal{J}(L-R)$ is similar to Eq. (24), we just need to change $A^f(R)$, $B^f(R)$, $\Phi_1^f(R)$, and $\Phi_2^f(R)$ to $A(R)$, $B(R)$, $\Phi_1(R)$, and $\Phi_2(R)$, where

$$B(R) = \sqrt{\xi^6(R) + 2\xi^3(R)\cos 2\beta\pi + 1}, \tag{30}$$

$$C(R) = \sqrt{\xi^8(R) - 2\xi^4(R)\cos 2\beta\pi + 1}, \tag{31}$$

$$\Phi_1(R) = -\arctan\frac{\xi^3(R)\sin 2\beta\pi}{1 + \xi^3(R)\cos 2\beta\pi}(+\pi), \tag{32}$$

$$\Phi_2(R) = \arctan\frac{\xi^4(R)\sin 2\beta\pi}{1 - \xi^4(R)\cos 2\beta\pi}(+\pi), \tag{33}$$

$$\xi(R) = \frac{R}{L - R}. \tag{34}$$

It is clear that when $R/L \to 0$, we have $B^f(R) \to B(R)$, $\Phi_1^f(R) \to \Phi_1(R)$, and $C^f(R) \to C(R)$, $\Phi_2^f(R) \to \Phi_2(R)$, so we do not need to consider such effect. But when R is comparable to L, the situation is very different. To illustrate, we plot $B^f(R)/B(R)$ in Fig. 5. From this figure, we find that when $R < 0.2L$, the difference between $B^f(R)$ and $B(R)$ is very small and we can ignore it, but when $R > 0.2L$, the difference becomes very big and cannot be ignored.

4. Conclusion

In summary, we get a general form of electron density inside metallic films. When x/L is very small, this form is reduced to the form for a half-infinite film. In contrast, when x is comparable to L, this general form becomes significantly different from the one for half
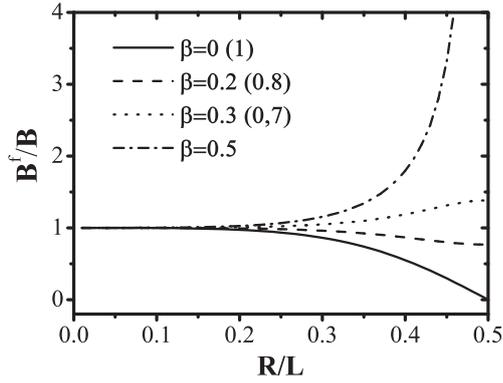
Fig. 5. B^f/B as a function of R/L for different values of $\beta = 0(1)$, 0.2(0.8), 0.3(0.7), 0.5.

infinite model. We are able to quantify this difference and find it oscillating with film thickness with a period of $\lambda_f/2$. This difference can be regarded as the result of interaction between two sets of Friedel oscillations originated from the two sides of the film. For Pb (111) films, the oscillations of interaction can be very robust because of the special value of d_0: λ_f. We find similar QSE in RKKY interactions inside films: when **R** is perpendicular to film surfaces, the RKKY interaction between two localized magnetic moments in a film should satisfy Eq. (24), and such effect cannot be ignored when $R > 0.2L$.

Acknowledgments

Appendix A

When $x \sim L$, with expansions

$$\frac{1}{L + 2\delta_n} = \frac{1}{L} - \frac{2\delta_n}{L^2} + \dots \tag{A.1}$$

$$\delta_n = \delta^{(0)} + \frac{n}{N}\delta^{(1)} + \left(\frac{n}{N}\right)^2 \delta^{(2)} + \dots, \tag{A.2}$$

we find that

$$n(x) - \frac{1}{2\pi L}\sum_{n=1}^{N}\left(k_f^2 - k_n^2\right) = \delta n_1(x) + \delta n_2(x) + \delta n_3(x) + O\left(\frac{\delta n_3}{L}\right), \tag{A.3}$$

where

$$\delta n_1(x) = -\frac{\pi}{2L^3}\sum_{n=1}^{N}\left[(N + \beta)^2 - n^2\right]\cos 2(n\theta + \phi_n),$$

$$\delta n_2(x) = \frac{2\pi}{L^4}\sum_{n=1}^{N}\left[\delta_N(N + \beta)^2 - \delta_n n^2\right]\cos 2(n\theta + \phi_n),$$

$$\delta n_3(x) = -\frac{6\pi}{L^5}\sum_{n=1}^{N}\left[\delta_N^2(N + \beta)^2 - \delta_n^2 n^2\right]\cos 2(n\theta + \phi_n),$$

$$\phi_n = \frac{n\pi\left(\delta_n - \delta^{(0)}\right)}{L + 2\delta_n}\left[1 - \frac{2\left(x + \delta^{(0)}\right)}{L + 2\delta^{(0)}}\right],$$

$$\theta = \frac{\pi\left(x + \delta^{(0)}\right)}{L + 2\delta^{(0)}}. \tag{A.4}$$

The summations in the above can be worked out explicitly. First of all, we have

$$f(\theta, \phi_i) = \sum_{i=1}^{N}\cos(2i\theta + 2\phi_i)$$

$$= -\frac{1}{2} - \frac{1}{2}\cot\theta\sin 2\phi_1 + \frac{\sin 2\left(N\theta + \frac{\theta}{2} + \phi_N\right)}{2\sin\theta}$$

$$- \frac{(\phi_N - \phi_{N-1})\sin 2(N\theta + \phi_N)}{2\sin^2\theta} + O\left(\frac{1}{L^2}\right), \tag{A.5}$$

where $f(\theta, \phi_i)$ means $f(\theta, \phi_1, \phi_2, \dots, \phi_N)$. Inserting Eq. (A.1) in the expression of ϕ_N and ϕ_{N-1}, we can find that $\phi_1 \sim O(1/L^2)$, and $\phi_N - \phi_{N-1} \sim O(1/L)$. Other summations can be expressed in terms of $f(\theta, \phi_i)$ and they are

$$\sum_{i=1}^{N} i^{2k}\cos(2i\theta + 2\phi_i) = \frac{(-1)^k}{2^{2k}}\frac{\partial^{2k}}{\partial\theta^{2k}}f(\theta, \phi_i),$$

$$\sum_{i=1}^{N} i^{2k-1}\cos(2i\theta + 2\phi_i) = \frac{(-1)^k}{2^{2k}}\frac{\partial^{2k-1}}{\partial\theta^{2k-1}}\lim_{\eta\to 0}\frac{\partial}{\partial\eta}f(\theta, \phi_i + \eta), \tag{A.6}$$

where k is a positive integer. With these relations, we can compute $\delta n_1(x)$, $\delta n_2(x)$, and $\delta n_3(x)$ and arrive at

$$n(x) = n_c + n_0\left\{\frac{3(1 - \beta)\eta^2(x)}{(2k_f x)^2}\cos 2[(k_f - \beta k_1)x - \gamma_N] + \frac{3\beta\eta^2(x)}{(2k_f x)^2}\cos 2\left[(k_f + (1 - \beta)k_1)x - \gamma_{N+1}\right]\right\}, \tag{A.7}$$

where

$$\eta(x) = \frac{\frac{\pi x}{L}}{\sin\frac{\pi x}{L}}, k_1 = \frac{\pi}{L + 2\delta_N}. \tag{A.8}$$

Note that for the computation leading to the above express we have ignored all terms of the order $O(1/L^{2+i})$. Because of this, some complicated computations need not be taken. For example, since we can prove

$$\sum_{i=1}^{N} i^n\cos(2i\theta + 2\phi_i) \sim O(L^n), \tag{A.9}$$

we can ignore $\delta n_3(x)$, which is of the order $O(1/L^3)$.

The constant term n_c in $n(x)$ can be determined by the electroneutrality in the middle of the film, which requires $v(x) - v(L/2) \sim O(1/L^i)$ ($v(x)$ is the electric potential). At $x = 2L/3$, we have

$$v\left(\frac{2L}{3}\right) - v\left(\frac{L}{2}\right) = \frac{\pi L^2}{18}(n_c - n_0) + 4\pi\int_{\frac{L}{2}}^{\frac{2L}{3}}\int_{\frac{L}{2}}^{x}[n(x') - n_c]dx'dx \sim O\left(\frac{1}{L^i}\right). \tag{A.10}$$

Because

$$\int_{\frac{L}{2}}^{\frac{2L}{3}}\int_{\frac{L}{2}}^{x}[n(x') - n_c]dx'dx \sim O\left(\frac{1}{L^2}\right), \tag{A.11}$$

we find

$$n_c - n_0 \sim O\left(\frac{1}{L^{2+i}}\right). \tag{A.12}$$

So, replacing n_c with n_0 and omitting some high order terms we can get the electron density expressed in Eq. (11).

To consider the influence of the approximate amplitudes of wave functions, we just need to expand $1/(L+l_n)$ with $1/L - l_n/L^2 + ...$ and express l_n (similarly to δ_n) as

$$l_n = l^{(0)} + \frac{n}{N} l^{(1)} + \left(\frac{n}{N}\right)^2 l^{(2)} + \ \ .... \tag{A.13}$$

With these expansions, we find that replacing L with $L+l_n$ in the amplitude of wave function just adds $O(1/L^3)$ terms in the final expression of electron density.

References

[1] J. Friedel, Nuovo Cim. 7 (suppl. 2) (1958) 287.
[2] P.T. Sprunger, L. Petersen, E.W. Plummer, E. Lagsgaard, F. Besenbacher, Science 275 (1997) 1764.
[3] M.F. Crommie, C.P. Lutz, D.M. Eigler, Nature 363 (1993) 524.
[4] M.F. Crommie, C.P. Lutz, D.M. Eigler, Science 262 (1993) 218.
[5] Y. Hasegawa, Avouris Ph, Phys. Rev. Lett. 71 (1993) 1071.
[6] M.C.M.M. van der Wielen, A.J.A. van Roij, H. van Kempen, Phys. Rev. Lett. 76 (1996) 1075.
[7] M. Schmid, W. Hebenstreit, P. Varga, S. Crampin, Phys. Rev. Lett. 76 (1996) 2298.
[8] A. Weismann, M. Wenderoth, S. Lounis, P. Zahn, N. Quaas, R.G. Ulbrich, P.H. Dederichs, S. Blugel, Science 323 (2009) 1190.
[9] B. Wu, Zhang Zhenyu, Phys. Rev. B 77 (2008) 035410.
[10] N.D. Lang, W. Kohn, Phys. Rev. B 1 (1970) 4555.
[11] E. Wahlström, I. Ekvall, H. Olin, L. Walldén, Appl. Phys. A Mater. Sci. Process. A66 (1998) S1107.
[12] P. Hyldgaard, M. Persson, J. Phys. Condens. Mater 12 (2000) L13.
[13] J. Repp, F. Moresco, G. Meyer, K.H. Rieder, P. Hyldgaard, M. Persson, Phys. Rev. Lett. 85 (2000) 2981.
[14] N. Knorr, H. Brune, M. Epple, A. Hirstein, M.A. Schneider, K. Kern, Phys. Rev. B 65 (2002) 115420.
[15] S. Nitya Nath, A. Sen, R. Prasad, Phys. Rev. B 76 (2007) 174417.
[16] A.T. Hindmarch, B.J. Hickey, Phys. Rev. Lett. 91 (2003) 116601.
[17] P. Bruno, C. Chappert, Phys. Rev. Lett. 67 (1991) 1602.
[18] N. Bloembergen, T.J. Rowland, Phys. Rev. 97 (1955) 1679.
[19] R. Sokel, W.A. Harrison, Phys. Rev. Lett. 36 (1976) 61.
[20] P. Czoschke, H. Hong, L. Basile, T.-C. Chiang, Phys. Rev. Lett. 91 (2003) 226801.
[21] P. Czoschke, H. Hong, L. Basile, T.-C. Chiang, Phys. Rev. B 72 (2005) 035305.
[22] D.C. Langreth, Phys. Rev. B 5 (1972) 2842.
[23] F.K. Schulte, Surf. Sci. 55 (1976) 427.
[24] R. Stratton, Phys. Letters 19 (1965) 556.
[25] R. Monnier, J.P. Perdew, Phys. Rev. B 17 (1978) 2595.
[26] M. Manninen, R. Nieminen, P. Hautojärvi, J. Arponen, Phys. Rev. B 12 (1975) 4012.
[27] K. Takahashi, T. Onzawa, PHys. Rev. B 48 (1993) 5689.
[28] M.A. Ruderman, C. Kittel, Phys Rev 96 (1954) 99.
[29] T. Kasuya, Prog Theoret Phys Kyoto 16 (1956) 45.
[30] K. Yosida, Phys Rev. 106 (1957) 893.
[31] C. Kittel, Quantum Theory of Solids, Wiley, New York, 1963 Chap. 18, formula 125.
[32] J.H. Van Vleck, Rev. Mod. Phys 34 (1962) 681.