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Inapplicability of the Sugiyama phase sum rule to very thin films

J. P. Rogers III, T. E. Feuchtwang, and P. H. Cutler
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

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The Sugiyama phase sum rule, derived for a free-electron model, implies that the Fermi energy of a thin film cannot be size dependent. This rule is shown to be invalid for very thin films ($L_z \lesssim 50$ Å) in a square-well model, since it depends on the incorrect assumption of local charge neutrality near the center of the film. The displacement of the potential barriers outward from the surfaces of very thin films in order to produce local charge neutrality in the interior is discussed. The size dependence found for the free-electron model is expected to persist in the presence of electron-electron interactions, though possibly with reduced magnitude.

In 1960 Sugiyama[1] derived a "phase sum rule" for a free-electron model, which relates the phase shifts of the electronic wave functions in a metallic film, due to the presence of surfaces, to the Fermi wave vector. This sum rule, which is analogous to the Friedel sum rule for impurity-induced phase shifts,[2] states that a certain average of the phase shifts, to be defined below, is equal to $\pi/4$. This result has been rederived and extended by Langreth,[3] Applebaum and Blount,[4] and Paasch and Wonn.[5] The validity of the phase sum rule has been accepted to such a degree that it has been used as a "consistency check" in the sense that if a theory is not consistent with the phase sum rule or its implications it is considered incorrect.[6-9] One of the implications of the rule is that, aside from small oscillations due to the discreteness of the eigenvalue spectrum,[10] the Fermi energy, E_F, of a thin film must equal its bulk value, E_F^0. This is shown explicitly by Paasch and Wonn.[5] This, in turn, implies that other quantities related to the Fermi energy, such as the electronic density of states and the superconductive transition temperature, do not exhibit size dependence in thin films. A key assumption in every derivation of the phase sum rule for a film (or "slab") geometry is that of "local charge neutrality," i.e., that in a region centered at the middle of the slab, the average electronic charge density is equal in magnitude to the average ionic charge density, or equivalently, to the *bulk* electronic charge density. It is the purpose of this Brief Report to show that for a free-electron, square-well model of a very thin film, such as considered by Sugiyama, the assumption of local charge neutrality is not valid, and therefore the phase sum rule is not applicable to such a system. Furthermore, the fact that local charge neutrality is not maintained is shown to imply that the Fermi energy *must* be thickness dependent. Hence, size effects in the electronic energy spectrum, the Fermi energy, and related quantities[17] should exist. As is discussed below, these effects are expected to occur even in the presence of electron-electron interactions, though possibly with a reduced magnitude.

The phase sum rule states that

$$\langle\eta\rangle \equiv (2/k_F^2)\int_0^{k_F} \eta(k_z)k_z dk_z = \pi/4 \ , \tag{1}$$

where the phase shifts, $\eta(k_z)$, are defined by

$$\psi(z,k_z) = A(k_z)\sin[k_z z + \eta(k_z)] \ . \tag{2}$$

The function $\psi(z,k_z)$ describes the asymptotic z dependence of the total wave functions, $\Psi(\mathbf{r},\mathbf{k})$, in the interior. The film is assumed to have a thickness L_z, and is located between the $z=0$ and the $z=L_z$ planes. The phase shifts and the normalization constants, $A(k_z)$, depend upon the precise form of the surface potential barrier. The assumption of local charge neutrality, used in deriving the sum rule for the slab geometry, requires that the film be thick enough that there exists a region sufficiently far from the surfaces for bulklike conditions to obtain. For a thick film this will certainly be the case, and the phase sum rule will be valid.

For a very thin film, however, no region is "very far" from the surface, and local charge neutrality need not be maintained in any part of the film. To demonstrate this we have calculated the electron density, $n(z)$, as a function of position, in a free-electron model where the electrons are in a square potential well of depth $V_z \equiv \hbar^2 k_{\text{top}}^2/2m$ and width L_z in the direction normal to the plane of the film. Periodic boundary conditions are imposed in the directions parallel to the film plane. In the z direction the boundary conditions are that $\psi(z,k_z)$ and its derivative $\partial\psi(z,k_z)/\partial z$ be continuous at the edge of the well, and that $\psi(z,k_z)$ go to zero as $z \rightarrow \pm\infty$. In this case[18] the z dependence of the wave functions in the interior of the well is given exactly by Eq. (2), with the phase shifts equal to $\sin^{-1}(k_z/k_{\text{top}})$. We emphasize that this model does not involve the truncation of the wave function at any distance outside the film. Thus overall charge neutrality, as distinct from local neutrality, is automatically satisfied as a consequence of the correct normalization of the wave functions. The electron density was calculated by numerically summing the expression

$$\begin{aligned} n(z) &= 2(L_xL_y/4\pi^2)\sum_{k_z}\int dk_x \int dk_y \,|\Psi(\mathbf{r},\mathbf{k})|^2 \\ &= (L_xL_y/2\pi)\sum_{k_z}(k_F^2-k_z^2)\,|\psi(z,k_z)|^2 \ , \end{aligned} \tag{3}$$

over the values of k_z, which are given by[18]

$$k_zL_z = n_z\pi - 2\sin^{-1}(k_z/k_{\text{top}}) \ . \tag{4}$$

In Fig. 1 the electron density is shown for a "square-well film" with a thickness of 30 Å, for three different values of the well depth. In this figure, the density is normalized to

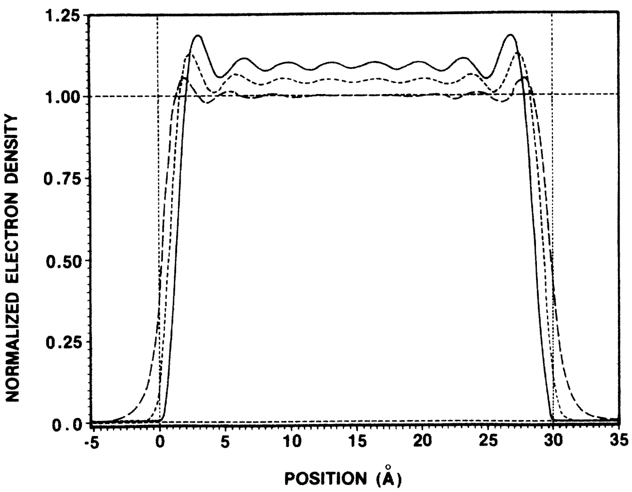

FIG. 1. The electron density for a free-electron, square-well model of a thin film is shown as a function of position for three values of the well depth, V_z. The film thickness is 30 Å. The number of electrons, per unit surface area, is the number in a 30-Å-thick slab in the interior of a bulk sample with $r_s/a_0=4$. The density is normalized to the average bulk value, $n^0 \equiv (k_F^0)^3/3\pi^2$, where k_F^0 is the bulk Fermi wave vector. The solid curve corresponds to $V_z=\infty$, the short-dashed curve to $V_z=10$ eV, and the long-dashed curve to $V_z=3.13$ eV. For the smallest well depth the topmost level in the potential well is occupied. The vertical dashed lines represent the location of the film surfaces and the barriers. The curves are *not* offset from the horizontal axis.

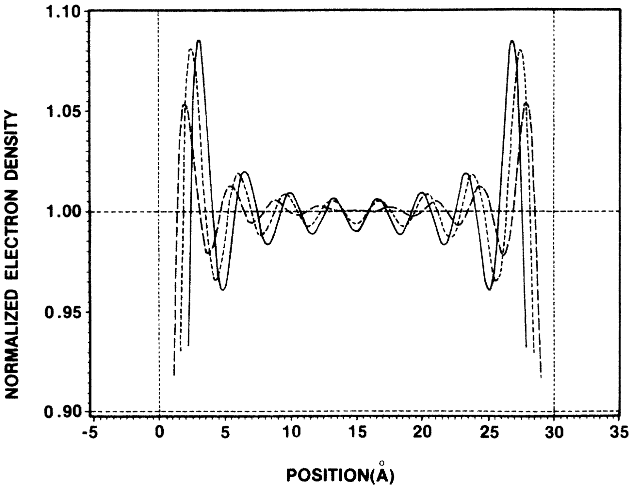

FIG. 2. The same data as in Fig. 1, *renormalized* to $k_F^3/3\pi^2$, where k_F is the Fermi wave vector in the film. The relationship between k_F and its bulk value, k_F^0, is given by Eq. (5).

the bulk density, $n^0=(k_F^0)^3/3\pi^2$, where k_F^0 is the bulk value of the Fermi wave vector. Several observations are appropriate. First, the Friedel oscillations in the density persist throughout the entire thickness of the film, showing that nowhere in the film do bulklike conditions exist. Second, the mean value of the density near the middle of the film is not equal to its bulk value, except in the special case ($V_z=3.13$ eV) in which the well depth is equal to the bulk value of the Fermi energy, as discussed below. Therefore, the key assumption of the phase sum rule is not valid. It follows that the sum rule does not hold, in general, for a very thin film in this model. As discussed below, this result also is expected for more general models in which electron-electron interactions are included.

In Fig. 2 the density is renormalized to $k_F^3/3\pi^2$, where k_F is the magnitude of the wave vector of the highest occupied state at $T=0$ K. It is evident that the mean value of the density in the central region of the film[19] is equal to $k_F^3/3\pi^2$. Since local charge neutrality requires that $k_F^3/3\pi^2$ equal $(k_F^0)^3/3\pi^2$, local charge neutrality will be maintained only if $k_F=k_F^0$, i.e., if the Fermi energy equals its bulk value. Thus the statement that E_F cannot be size dependent, rather than being a novel prediction of the phase sum rule, is simply an equivalent way of stating the assumption (total mean local charge neutrality) upon which the rule is based. Therefore, it is clear that the sum rule is valid only under conditions for which E_F is *not* size dependent. *Thus the phase sum rule cannot be used to show that size effects in the Fermi energy and related quantities do not exist. Conversely, the fact that local charge neutrality is not maintained necessarily implies that $k_F \neq k_F^0$, i.e., that the Fermi energy* is *size dependent.*

We have shown[12] that in the square-well model k_F is approximately given by

$$k_F = k_F^0 + \pi/4L_z - (1/2L_z) \times [(2-\lambda^0)\sin^{-1}(\lambda^0)^{-1/2} + (\lambda^0-1)^{1/2}] \ , \qquad (5)$$

where $\lambda^0 \equiv (k_{\mathrm{top}}/k_F^0)^2$. In deriving this equation we neglected the small-amplitude oscillations[11-13] in the Fermi energy which arise from the discreteness of the eigenvalue spectrum. Equation (5) indicates that E_F equals its bulk value only when (a) the film thickness, L_z, is sufficiently large; or (b) the depth of the well is equal to the bulk value of the Fermi energy. (In the latter case[12] $E_F=E_F^0=V_z$, which implies that the well is full, i.e., the topmost energy level in the well is occupied.) Thus local charge neutrality is maintained only when either condition (a) or (b) is satisfied. Therefore *the phase sum rule—and its "prediction" that the Fermi energy cannot be size dependent—are valid only when the film is sufficiently thick, or when the well depth equals the bulk value of the Fermi energy.* When neither of these conditions occurs the phase sum rule is not valid, and the Fermi energy and related quantities exhibit size effects.

The phase sum rule may be formally imposed on a film by a method first proposed by Bardeen,[20] and which is sometimes discussed independently of the phase sum rule. This method consists[1,20-23] of moving the potential barriers out a certain distance (on the order of a lattice constant) from the surfaces[24] of the film. It assures local charge neutrality, and thus eliminates size effects. For a given bulk average electron density, $n^0=(k_F^0)^3/3\pi^2$, this distance is

$$d = 3\pi/8k_F^0 - (3/4k_F^0) \times [(2-\lambda^0)\sin^{-1}(\lambda^0)^{-1/2} + (\lambda^0-1)^{1/2}] \ , \qquad (6)$$

where λ^0 is defined as in Eq. (5), and the last two terms vanish if the well is infinitely deep. Equation (6) has been referred to as a "charge conservation law," since like the sum rule, it is based on the idea of local charge neutrality. The displacement of the potential walls introduces an extra phase into the wave functions, which increases the total phase shift to the amount necessary to obey the sum rule. However, for a very thin film, this displacement of the potential barriers is not justified, since there is no physical reason for requiring such a film to exhibit local charge neutrality. For a thick film the procedure, while justified, is unnecessary, since in such a film local charge neutrality exists regardless of whether the potential barriers are displaced or not. Furthermore, for the exceptional case in which the topmost level in the well is occupied, Eq. (6) yields $d = 0$, so that no displacement of the barriers is required in order to achieve local charge neutrality.

It is thus clear that the phase sum rule and the related "charge conservation law" are, in general, invalid for very thin films in the square-well model, since they depend on the generally incorrect assumption of total local charge neutrality. Application of these conditions to such films leads to an unjustified and unphysical elimination of size effects in the electronic energy spectrum and related quantities. For the exceptional case in which the top level in the square potential well is occupied, the sum rule and the "charge conservation law" are valid, but irrelevant, since their application has no effect on the system.

The phase sum rule and the "charge conservation law" have been applied to metallic films in order to show that the Fermi energy must be equal to its bulk value,[5-7,9] and that the superconductive transition temperature cannot be size dependent.[7,8] Clearly, such conclusions are not justified for very thin films. The sum rule and "charge conservation law" have also been used in calculations of the surface energy in the square-well model.[1,5,21,22] Thus some of the results of these investigations may not be valid for very thin films; in particular, the formulas derived in these references may underestimate the surface energy[25] calculated within this model.

We note that the existence of size effects in a thin film may be interpreted as the propagation of the disturbance of the electron gas, caused by the surfaces, into the interior region of the film. It can be argued that in a 30-Å-thick film this perturbation is expected to be screened out within a few angstroms of each surface and therefore should not affect the central region of the film. However, calculations of the polarizability of very thin films[26] indicate that the dielectric function of such films may be substantially reduced relative to the bulk value of the dielectric function. This suggests the persistence of size effects in very thin films, even when screening is taken into account.

It is recognized that the free-electron model gives rise to a large electron density in the interior of a very thin film, due to its neglect of the Coulomb repulsion between the electrons. Inclusion of the repulsive Coulomb interaction will produce a displacement of the electrons outward from the center of the film, thus lowering the mean electron density in the interior. This may, in turn, lead to a decrease in the magnitude of the size effects. We note that the Sugiyama sum rule and the barrier displacement procedure can be thought of as an *ad hoc* attempt to compensate for the neglect of the Coulomb repulsion of the electrons, since displacing the barriers reduces the electron density in the interior. We believe, however, that the sum rule and the barrier displacement procedure, by producing *complete* local charge neutality, probably overcompensate for the effect of the Coulomb repulsion. For extremely thin films, there is no *a priori* reason to expect the Coulomb repulsion to lead to complete local charge neutrality in the film interior, which would imply that size effects are completely eliminated.

Indeed, size effects in the work function have been predicted in films several monolayers thick in theoretical investigations which take into account the atomistic nature of the films.[27] It is likely that these size effects result not only from the inclusion of the ion cores into the problem but also from the confinement of the itinerant electrons by the film surfaces. If this is the case, size effects should appear in calculations which include electron-electron interactions, and which replace the ions with a positive jellium. Calculations to test this conjecture using the density functional formalism are in progress.

In conclusion, the phase sum rule and the procedure of displacing the potential barriers are not valid for very thin square-well films ($L_z \lesssim 50$ Å), since they depend on the incorrect assumption of total local charge neutrality. The application of this assumption to a thin film reflects the erroneous notion that all films must exhibit bulklike behavior in their interior, regardless of how thin they are. The phase sum rule and the barrier displacement procedure are valid only for films thick enough that size effects in the electronic energy spectrum are already negligible, and for the exceptional case in which the top level in the potential well is occupied.

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and may have been observed in the superconducting properties of thin films (Ref. 16). In this paper we restrict our attention to the size dependence of the nonoscillatory component of quantities such as E_F, upon which these oscillations are superimposed, since it is the existence of the nonoscillatory component that has been questioned.

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