Comparison of calculations of dynamical screening at jellium surfaces

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We compare recent computations of dynamical screening at jellium surfaces. Both published results from different groups and new calculations are plotted in a common fashion to exhibit their extent of agreement about qualitative features and quantitative values. A physical picture for a surface-driven Friedel oscillation in the induced density is presented. This particular oscillation is especially strong near the resonance in the d parameter.

There has been a recent resurgence of interest in computing the screening response of metal surfaces to optical fields. In this paper we compare the results found by several groups,[1-6] who claim to have reproduced and extended the pioneering calculations of Feibelman.[7,8] We believe that such a comparison is useful because each group has formulated the computational task in different ways. By plotting their separate results together, one can readily see what features they have in common and get a sense of the numerical uncertainties.

We discuss here only results for a jellium model whose density in bulk is parametrized by $r_s=3$. The basic quantity of interest is the induced screening charge density $\delta\rho$ at a single, flat surface in response to a uniform electric field at frequency ω, applied normal to the surface. We restrict ω to be less than ω_p, the bulk plasma frequency. Many of the physical consequences of this screening response do not require the full $\delta\rho$, but instead only the ratio of its first to zeroth moment:[8-12]

$$d_\perp(\omega)=\int dx\, x\, \delta\rho(x) \Big/ \int dx\, \delta\rho(x)\ . \tag{1}$$

Here the integrations run along the coordinate normal to the surface, x, and we have introduced Feibelman's d parameter notation for the ratio of the moments.[13,8,9,14] The other d parameter for a jellium surface, $d_\parallel$, has been made to vanish by choosing the origin for x at the edge of the jellium, which occupies the half-space $x\geq 0$.

We begin by showing in Fig. 1 results for both the real and imaginary parts of $d_\perp(\omega)$ as calculated in the random-phase approximation (RPA). Four separate calculations are illustrated, of which three are in reasonable quantitative agreement where they overlap in frequency, while the fourth has significant differences. The three calculations that essentially agree are each done quite differently. The method used by Kempa and Schaich[6] is largely developed in wave-vector space, while those used by Feibelman[7,8] or Liebsch[5] are based in real space. These latter two differ in their numerical treatment of the long-ranged Friedel oscillations in $\delta\rho$. Only Liebsch's calculations give stable results over the whole range $0\leq\omega<\omega_p$. Feibelman's points do not go below $0.6\omega_p$, while the small absolute errors in the results of Kempa and Schaich[6] make their predictions for the imaginary part of $d_\perp(\omega)$ increasingly unreliable as $\omega\rightarrow 0$.

The fourth set of results shown in Fig. 1 is taken from Ref. 2, and to be fair, does not quite correspond to the same physical model numerically solved by the first three. Specifically, they (i) treat a slab geometry of width 70 Å rather than a semi-infinite substrate, (ii) use infinite barriers outside the slab in order to make the one-body eigenstates for motion normal to the surface all have discrete eigenvalues, and (iii) introduce a broadening in energy denominators which amounts to $\hbar\omega_p/20$. The first and third of these changes are the source of the noticeable differences in Fig. 1. We return to this point below, but note here that we confirmed our claim by setting up a code analogous to that of Ref. 2 and varying the extra constraints.

Almost the same general comments apply to the results in Fig. 2, which show three separate calculations of $d_\perp(\omega)$ done in the time-dependent local-density approximation (LDA). These evaluations include the effects of exchange and correlation in the same (approximate) way for the ground state and for the dynamic response. This extension of consistently treating exchange and correlation represents the recent formal improvement over Feibelman's random-phase-approximation (RPA) calculations. It makes the results merge with the static response calculated by Lang and Kohn[15] and ensures that certain sum rules will hold.[16] The quantitative differences between the various calculations are somewhat larger than in Fig. 1, which may in part be due to the fact that each group used a different functional form for the exchange-correlation energy. Gies and Gerhardts[4] used the equations of Gross and Kohn,[17] together with those of Vosko,

Wilk, and Nusair.[18] Liebsch used the Wigner interpolation formula,[19] and Kempa and Schaich use the parametrization of Hedin and Lundqvist.[20]

We next discuss four different structures that are of interest in the curves shown in Figs. 1 and 2. Begin with the limit $\omega \to \omega_p$, where, in the absence of any bulk damping, we expect the real part of $d_\perp$, $\mathrm{Re}(d_\perp)$, to diverge since it becomes possible to excite a bulk plasmon, initially of infinite wavelength. A rapid increase above $0.9\omega_p$ is evident in the results of Liebsch or of Kempa and Schaich but one does not have enough points to determine its functional form. In simple hydrodynamic models[14,21] $d_\perp$ grows as $(\omega_p - \omega)^{-1/2}$, which determines the plasmon's penetration length. However, since any reasonable bulk damping will cause both this length and $d_\perp$ to saturate, the results of Gies and Gerhardts near ω_p may be closer to what one should expect experimentally.

A similar difficulty arises at the opposite extreme, $\omega \to 0$, where the quantity of interest is the limiting slope of the imaginary part of $d_\perp$, $\mathrm{Im}(d_\perp)$. There is about a factor of 2 difference between the LDA slope predicted by Liebsch[5] and that by Gies and Gerhardts,[4] and a similar discrepancy exists for other choices of r_s. We feel the difference is not due to numerical errors in either calculation but instead is a consequence of distinct physical models. As $\omega \to 0$ the discrete spectrum of states for normal motion used by Gies and Gerhardts would in the absence of damping lead to a discrete absorption spectrum in response to a uniform field. One can suppress the resulting spiky structure in $\mathrm{Im}(d_\perp)$ by replacing $\omega \to \omega + i\gamma$, but this mathematical step also introduces new (bulk) mechanisms of energy absorption which can either add to or subtract from (in the sense of interference[22]) the contributions already present. In the low-frequency limit these changes are apparently significant. The clearest evidence of the quantitative influence of γ is in RPA calculations for the infinite barrier model,[2] where $\mathrm{Im}(d_\perp)$ is positive for $\omega < \omega_p$ if $\gamma \neq 0$, while one can prove that $\mathrm{Im}(d_\perp)$ must be negative over this range for any jellium model with no bulk damping.[8] The open question of what precise value of γ to use should wait at least until the incorporation of band-structure effects into the response calculations.

The next structure we briefly consider is, like the limiting slope of $\mathrm{Im}(d_\perp)$, also below the range of Feibelman's original calculations. It is associated with the threshold for photoemission, and appears as a slight dip in $\mathrm{Re}(d_\perp)$ and a weak shoulder in $\mathrm{Im}(d_\perp)$. When $r_s = 3$ the struc-

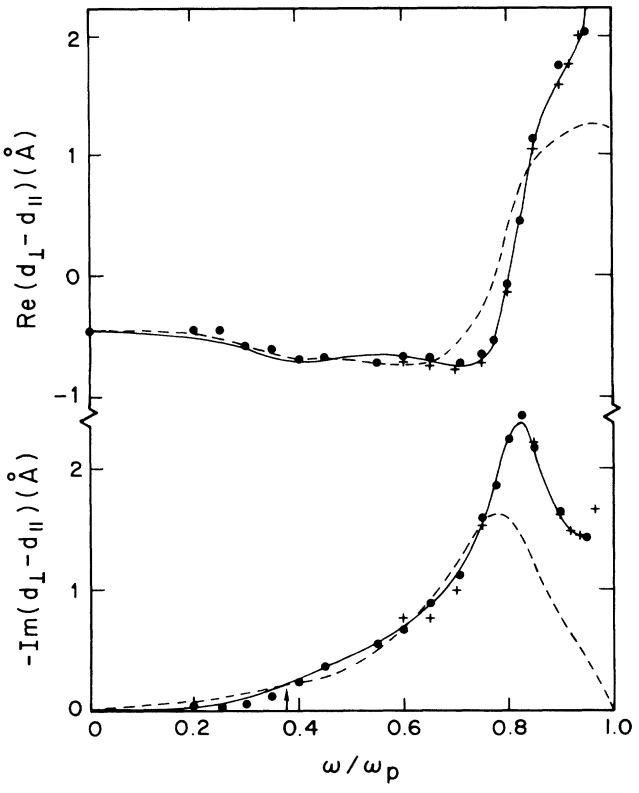

FIG. 1. RPA calculations of $d_\perp$ in angstroms vs frequency for $r_s = 3$. Both real and imaginary parts of $d_\perp$ are shown. The solid curve is from Ref. 5, the dashed curve from Ref. 2, the +'s are from Ref. 8, and the dots are new calculations from the code of Ref. 6. The arrow on the abscissa locates the threshold for photoemission.

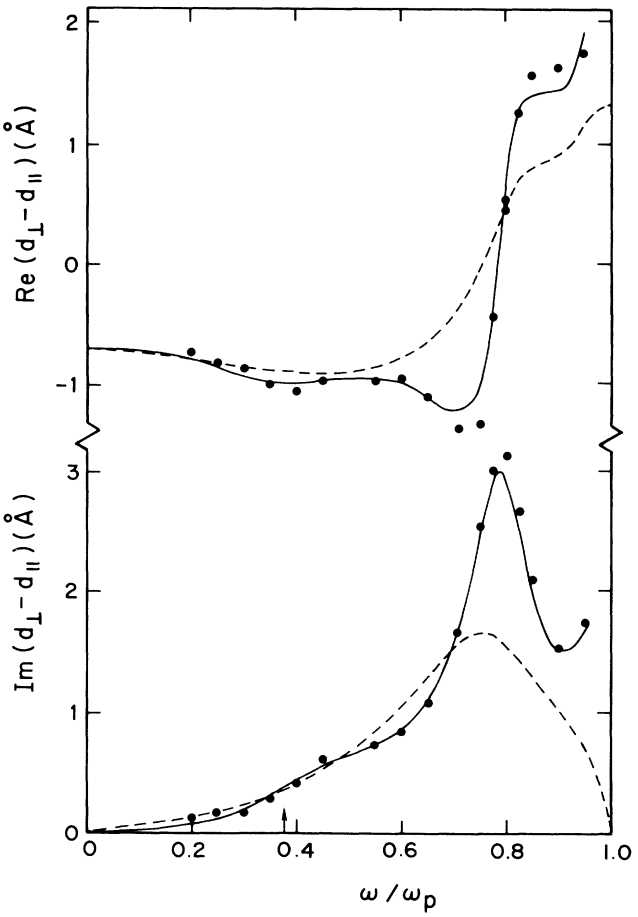

FIG. 2. LDA calculations of $d_\perp$ in angstroms vs frequency for $r_s = 3$. Both real and imaginary parts of $d_\perp$ are shown. The solid curve is from Ref. 5, the dashed curve from Ref. 4, and the dots are new calculations from the code of Ref. 6. The arrow on the abscissa locates the threshold for photoemission.

ture is fairly weak and is not even obvious in the calculation by Gies and Gerhradts,[4] being smeared out by γ. For smaller r_s the threshold is a smaller fraction of ω_p and the structure is more evident;[5,6] while for larger r_s it disappears in the strong structure near $0.8\omega_p$. Since the rise in $\mathrm{Im}d_\perp$ starts below threshold it cannot be attributed solely to photoemitted electrons, but must also have a significant contribution from absorption into final states that propagate into the bulk of the metal.

The last structure in $d_\perp$ we discuss is the largest and has provided a notable success in comparisons with experiment.[23-25] It consists of the sharp peak in $\mathrm{Im}(d_\perp)$ for ω near $0.8\omega_p$, and the associated rapid switch of $\mathrm{Re}(d_\perp)$ from outside to inside the jellium edge. All of the calculations illustrated in Figs. 1 and 2 show evidence for this structure, although those of Gies *et al.*[1-4] have it broadened somewhat more than one would expect from the size of their bulk damping term, $\gamma=0.05\omega_p$. The physical origin of this structure is still under debate. Various interpretations have been suggested and we refer the reader to the original calculations[1-8] as well as to other papers[26,27] and their references for further discussion. Here we just note that the inclusion of exchange and correlation at $r_s=3$ in the dynamic response only slightly shifts and sharpens the structure. Hence the existence of the structure can be usefully discussed at the RPA level. On the other hand, the resonance at $0.8\omega_p$ does depend very sensitively on the detailed profile of the ground-state electron distribution at the surface. It is remarkable that there is no evidence for the structure in calculations at the same bulk r_s for either the infinite barrier model[2,28] or a finite potential step barrier model.[2,6]

The final feature we discuss is also associated with the $0.8\omega_p$ structure, but is not apparent in Figs. 1 and 2. It concerns the strength and frequency of the Friedel oscillations of $\delta\rho$. These become quite pronounced there as is evident in plots[5,6] of $\delta\rho$ versus x for various ω. We show in Fig. 3 the results at $\omega=0.8\omega_p$ for $r_s=3$. The oscillation frequency is quite different from its static value of $2k_F$, where $k_F=1.21$ Å^{-1} is the Fermi wave vector, and the decay of the oscillation amplitude into the bulk is very slow.

To examine the source of these oscillations in real space, it is useful to study $\delta\rho$ in Fourier space, which for some of the computer codes is where, in fact, it is originally determined.[1-4,6,28,29] We show in Fig. 4 plots of the cosine Fourier transform of the same $\delta\rho$ shown in Fig. 3. The origin for the cosine transform is $L=7.9$ Å outside the jellium edge where $\delta\rho(x)$ is negligible. To have a sense of what to expect from the main peak of the reduced density, imagine that $\delta\rho(x)$ is a real-valued Gaussian,

$$\delta\rho(x)\sim e^{-(x-x_0)^2/\Delta^2}, \tag{2}$$

which implies for $\Delta \ll L$ that

$$\delta\rho(q)\sim\cos(q\bar{x}_0)e^{-(q\Delta)^2/4}, \tag{3}$$

where $\bar{x}_0=x_0+L$.

From Fig. 3 we see that $\bar{x}_0$ is roughly 8 Å while Δ is less than 2 Å. The dependence of Eq. (3) is crudely evident in Fig. 4, but of greater interest are the deviations from this simple behavior, since they give information on the Friedel oscillations.[30] In particular there is a rapid variation in the transformed $\delta\rho$ for wave vectors just above what we denote by q_s. This critical wave vector may be written as

$$\hbar q_s=\sqrt{2mV}-\sqrt{2m(V-\hbar\omega)}, \tag{4}$$

where V is the total height of the surface potential-energy barrier. For $V-E_F<\hbar\omega<V$ with E_F the Fermi energy,

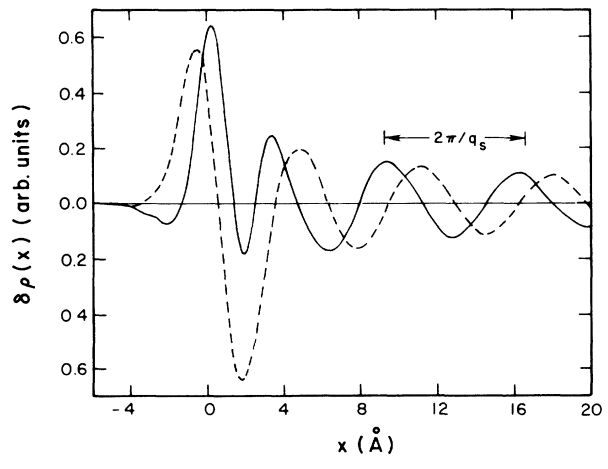

FIG. 3. LDA calculation of the induced charge density vs normal coordinate at $\omega/\omega_p=0.8$ for $r_s=3$. The jellium lies in $x>0$. The real (imaginary) part of $\delta\rho(x)$ is drawn with a solid (dashed) line.

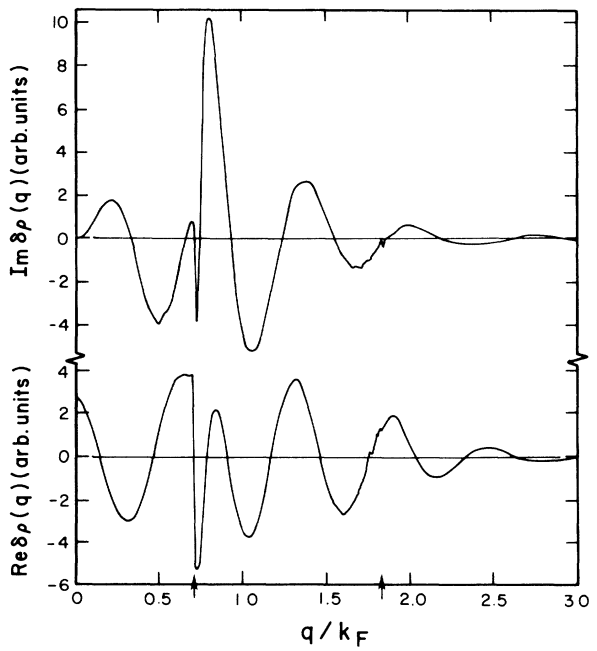

FIG. 4. Cosine Fourier transform of the induced charge density shown in Fig. 3. Both real and imaginary parts of $\delta\rho(q)$ are shown. Along the abscissa we note the location of the critical wave vectors q_s and $\bar{q}_s$.

q_s is a solution of

$$\hbar^2 k^2/(2m)+\hbar\omega=\hbar^2(k+q_s)^2/(2m)=V \tag{5}$$

subject to

$$0<|k|<k_F\ . \tag{6}$$

For the case shown in Fig. 3, $q_s=0.71k_F=0.86$ Å^{-1}, corresponding to a wavelength of 7.3 Å. The physical interpretation of these equations is that $\hbar q_s$ (and $\hbar\omega$) are the momentum (and energy) transferred to an electron which jumps from an occupied orbital to an unoccupied one at the vacuum level. The orbitals here are for motion normal to the surface; the plane-wave character of the eigenstate for motion parallel to the surface is unchanged by the transition. There is a second positive solution of Eqs. (5) and (6) which we write as

$$\hbar\bar{q}_s=\sqrt{2mV}+\sqrt{2m(V-\hbar\omega)}\ . \tag{7}$$

For the case of Fig. 3, $\bar{q}_s=1.83k_F=2.21$ Å^{-1}; but the corresponding k is negative and there is only a slight jitter in the transform near $\bar{q}_s$ which does not significantly affect the oscillations in real space.

The code of Ref. 6 is written to specifically allow for possible singular structure at q_s and $\bar{q}_s$, as well as at other wave vectors associated with the (bulk) Fermi surface,[29,31,32] e.g., the boundary points in q at fixed ω of the electron-hole pair continuum. For ω near $0.8\omega_p$ the strongest structure is associated with q_s for reasons that are not clear. Still it is interesting that the surface-sensitive resonance in $d_\perp$ and the amplitude of the surface-driven Friedel oscillations are coupled. Perhaps future analysis will be able to establish whether this correlation is causal or accidental.

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