

Approximate solution for the electronic density profile at the surface of jellium

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A simple family of trial functions for the electronic density at the surface of jellium, which accounts for Friedel oscillations and incorporates the Budd-Vannimenus theorem, is proposed. The free parameters are determined by energy minimization. Model calculations give good results for the work function and for the induced surface charge in the presence of an external field.

INTRODUCTION

An advantage of the Hohenberg-Kohn-Sham¹ formalism for an electronic plasma is the fact that the energy of the system can be written as a functional of the electronic density $n(x)$ alone. Since this energy attains its minimum at the true electronic density, it is suggestive to look for approximate solutions by choosing a suitable class of trial functions with several undetermined parameters, and to minimize the energy within that family. Indeed, the first realistic calculation of the jellium work function by Smith² employed a simple, one-parameter family of trial functions. Since this approach gave good results compared with the subsequent exact solution by Lang and Kohn,³ similar sets of trial functions were employed in studies on related problems.⁴ Recently, this approach has been used in several theories of the metal/solution interfaces.⁵⁻⁷

In this paper, we present a simple two-parameter class of trial functions which, in contrast to the functions commonly used, accounts both for Friedel oscillations and for the Budd-Vannimenus theorem⁸ and which reproduces the results of Lang and Kohn remarkably well.

THE TRIAL FUNCTIONS

From the general properties of an electronic plasma, and from the exact solution of the problem, one knows that the electronic density $n(x)$ drops off roughly exponentially on the vacuum side ($x > 0$) of the jellium edge, and that it tends towards the bulk value n_+ with superimposed Friedel oscillations on the metal side ($x < 0$). We therefore use the following family of trial functions, which is a generalization of the one employed by Smith:²

$$n(x) = n_+ \begin{cases} 1 - Ae^{\alpha x} \cos(\gamma x + \delta) & \text{for } x < 0, \\ Be^{-\beta x} & \text{for } x > 0. \end{cases} \quad (1)$$

Friedel oscillations decay as $1/x^2$ and have a wave number of $2k_F$. This parametrization does not have this asymptotic behavior. However, as will be seen below, the density with the parameters chosen the manner outlined does have the correct amplitude and frequency in the im-

portant interfacial region.

The six undetermined parameters A , B , α , γ , and δ must satisfy the following relations: continuity of $n(x)$

$$1 - A \cos \delta = B, \quad (2a)$$

continuity of $n'(x)$

$$A(\gamma \sin \delta - \alpha \cos \delta) = -\beta B, \quad (2b)$$

charge balance

$$\frac{A(\alpha \cos \delta + \gamma \sin \delta)}{\alpha^2 + \gamma^2} - \frac{B}{\beta} = \frac{\sigma}{n_+}, \quad (2c)$$

and the half-moment condition (Budd-Vannimenus)⁸

$$-\frac{n_+ A}{(\alpha^2 + \gamma^2)^2} [(\alpha^2 - \gamma^2) \cos \delta + 2\alpha \gamma \sin \delta] = h, \quad (2d)$$

where σ is the charge density on the jellium surface, and h is the left half-moment calculated in the Wigner approximation

$$h = \frac{\sigma^2}{2n_+} - \frac{k_F^2}{2} \left[0.4 - 0.0829r_s - \frac{0.0796r_s^3}{(r_s + 7.8)^2} \right]. \quad (3)$$

$k_F = (3\pi^2 n_+)^{1/3}$ is the Fermi momentum, $r_s = (3/4\pi n_+)^{1/3}$, and atomic units are used throughout.

By choosing A and B , say, as free parameters, the system of Eqs. (2) is easily transformed into a system of two nonlinear equations for α and γ , which has to be solved numerically; the remaining two parameters can then be calculated directly from the others. The free parameters are determined by minimizing the surface energy. With an efficient minimization program, convergence is fairly rapid for densities $n_+ \geq 5 \times 10^{-3}$; only for very low densities it is somewhat slow. For our calculations, we have used the energy functional given by Smith² plus the second-order gradient term for the kinetic energy as derived by Ma and Sahni.⁹ The latter term is important; its omission leads to work functions that are substantially too small.

RESULTS OF MODEL CALCULATIONS

We have performed model calculations both for uncharged and charged jellium surfaces. Figure 1 shows an example of the electronic density that we obtained for an uncharged surface and the results of the exact calculation.³ In our calculations, the Friedel oscillations are somewhat less pronounced, but the first maximum is almost exactly at the same position. The overall agreement is good considering that only two parameters are employed.

The jellium work function is a sum of the three terms: the bulk chemical potential, the potential drop between the metal bulk and the jellium edge, which is determined by the half-moment condition, and the potential drop between the jellium edge and the vacuum at infinity. In our calculation, the first two terms are exact, and only the third term is calculated through energy minimization. The resulting work functions compare well with those of Lang and Kohn (see Fig. 2); they are substantially better than the Smith values, and also compare well with those obtained by Sahni *et al.*¹⁰ in the so-called linear potential approximation.

With our trial functions, it is easy to investigate the effect of an external field on the jellium surface. Figure 3 shows the variation of the electronic density $\delta n(x)$ induced by a sheet with a small charge density situated at infinity. The result again agrees quite well with the exact solution. The position of the main maximum and the main minimum are reproduced well; they are somewhat more pronounced in our approximation, while the amplitude of the minor oscillations is reduced. Note that for small σ , the left half-moment in $x < 0$ is unchanged; this feature is not found in trial functions that have no Friedel oscillations, and that do not obey the Budd-Vannimenus theorem.

The center of mass x_0 of the induced surface charge lies in front of the jellium edge. Since x_0 is also the effective image plane for a charge situated outside of the jellium, this has the interesting consequence that a metal

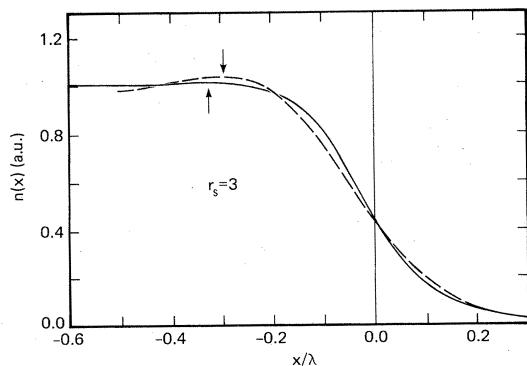


FIG. 1. Electronic density at the jellium surface for zero charge, and $r_s = 3$. Solid line, our calculation; broken line, Lang and Kohn. $\lambda = 2\pi/k_F$ is the Fermi wavelength. The arrows give the location of the maxima.

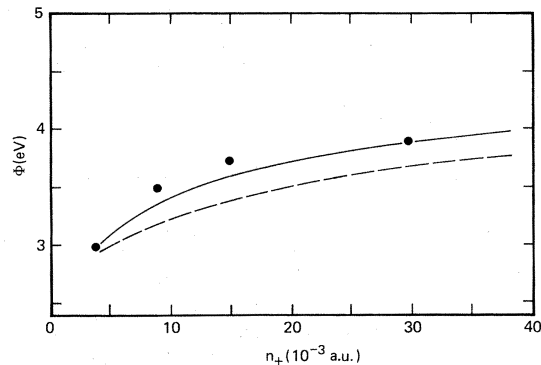


FIG. 2. Electronic work function in dependence of the bulk electronic density. Solid line, our calculation; broken line, Smith; solid circles, Lang and Kohn.

capacitor composed of two plates of the same jellium would have an effective plate separation which is smaller than the physical separation by $2x_0$.^{3,11} Since x_0 is typically of the order of 0.5 Å, this effect is not observable with real metal capacitors. There is, however, a system where this effect seems to be important: The double layer at the interface between a metal and a concentrated inert electrolyte acts like a capacitor with an effective plate separation of about 3 Å. Models of the interface which consider the metal to be a perfect conductor, and which consider the electrolyte to be an ensemble of hard-sphere ions and dipoles, predict capacities which are considerably too low.¹² This can be explained by the fact that the effective image plane is in front of the metal surface, and the effective plate separation smaller.⁷

Calculated values for the center of mass x_0 at small charge densities are given in Table I; again the agreement with Lang and Kohn is good. For higher charges, we define x_0 as a differential quantity, so that it gives the position of the image plane for the charge variation

$$x_0 = -\frac{d}{d\sigma} \int_{-\infty}^{\infty} x \delta n(x) dx = \frac{\sigma}{n_+} - \frac{d}{d\sigma} \int_0^{\infty} x \delta n(x) dx, \quad (4)$$

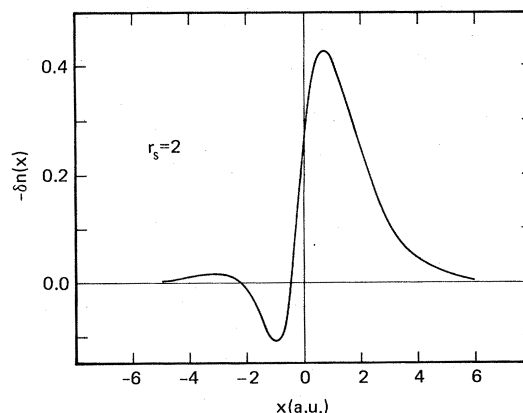


FIG. 3. Induced surface charge density for $r_s = 2$.

TABLE I. Effective-image-plane position for small excess charge.

r_s (a.u.)	x_0 (Å)	x_0^a (Å)
2	0.85	0.85 ± 0.03
3	0.75	
4	0.65	0.69 ± 0.1

^aLang and Kohn values.

where we have made use of the Budd-Vannimenus theorem to reexpress the left half-moment. Note that the derivative of the right half-moment gives the dominant contribution for small σ , and is necessarily negative, so that at least for small charge densities, the center of mass is positive. Figure 4 shows the variation of x_0 with σ . Over the investigated range x_0 decreases with increasing σ . The same trend has been observed by Theophilou and Modinos¹¹ and by Partenskii and Smorodinskii.⁴ This indicates that it is easier to pull electrons out of the metal by an electric field than to push them in. At sufficiently large negative fields, field emission would occur, which is not incorporated in our model; this seems, however, to be the reason why x_0 becomes unphysically large at higher negative surface charges for low electronic densities.

CONCLUSION

This simple two-parameter trial function which we have presented in this paper gives good results for the jellium surface in the vacuum. It seems particularly suited for the investigation of charged surfaces, and may also be

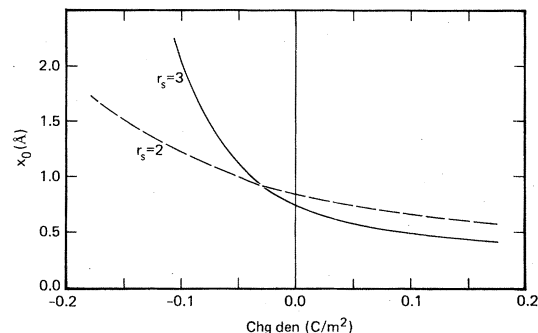


FIG. 4. Effective-image plane position as a function of the excess surface charge.

of use in more complicated systems such as electrochemical interfaces or adsorbates on metal surfaces.

An alternative to seeking an approximation solution to the exact jellium problem is, of course, to seek exact solutions to an approximate potential; the latter approach has been pursued by Sahni *et al.*¹⁰ Depending on the system under investigation, and on one's taste, either method may seem more convenient.

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