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Structure and surface tension of the liquid-vapor interface of simple metals: A theoretical approach

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We present a theory for the surface tension and the density profile of simple liquid metals. It is based on the perturbation expansion to second order in the electron-ion pseudopotential. This method is capable of describing the surface structures using the hard-sphere fluid as a reference system for the ions. The results for the alkaline metals are very sensitive to the parametrization of the ionic profile used in the variational calculation. On the other hand, for the polyvalent metals the calculated surface tension is in acceptable agreement with experiment and it is almost independent of the choice of the ionic-density-profile parametrization.

I. INTRODUCTION

Several theoretical approaches have appeared in the last two decades giving a microscopic description of the liquid-metal surface. In the early stages the study of the metal surface concentrated on the electronic aspect of the problem. These methods,[1] based on jellium models, replace the discrete ions by a uniform step distribution of positive charge. The jellium model is appropriate for studying solid metal surfaces although it is necessary to introduce the effect of discrete ions via a first-order perturbation theory to obtain good results in system with high electronic density. In order to obtain a more realistic description of the surface, Allen and Rice[2] modified those methods slightly, including the elastic energy of jellium, and they determined self-consistently the positive continuum jellium and electron distributions. They found very poor values for the surface tension, and, moreover, the ionic profile followed the electronic oscillations in order to decrease the electrostatic energy.

The opposite viewpoint was adopted by Evans and Kumaravadiviel.[3] They studied the problem concentrating on the ions and developing a pseudoatom theory based on a model ionic Hamiltonian,

$$H = \sum_i \frac{P_i^2}{2M} + \sum_i U(n(\mathbf{r}_i)) + \tfrac{1}{2}\sum_{i,j}[\phi(\mathbf{R}_{ij}, n(\mathbf{r}_i)) + \phi(\mathbf{R}_{ij}, n(\mathbf{r}_j))], \qquad (1)$$

which describes the motion of ions interacting with each other via the effective potential $\phi(\mathbf{R}, n)$ equal to the pair potential for a bulk metal of electronic density $n(\mathbf{r})$. $U(n(\mathbf{r}))$ represents the self-energy of a pseudoion surounded by its cloud of conduction electrons of local density $n(\mathbf{r})$. Although the variational calculation of the surface tension of several liquid metals, with parametrized exponential ionic density profile, gives reasonable agreement with the experiment, this approach does not lead to information about the electronic degrees of freedom and ignores the electrostatic contribution. In other words, it is not clear how these pseudoatom models are justified from a microscopic point of view. Mon and Stroud[4] and Wood and Stroud[5] studied the surface properties of liquid metals, treating them effectively as one-component fluids. They used techniques based on the classical density-functional formalism, similar to those applied to the study of insulating liquids. These models have the same difficulties as the pseudoatom model.

Lately methods have appeared that treat both the electrons and the ions at the same level. Evans and Hasegawa[6] and Amokrane *et al.*[7] took the first steps in this direction by including the effects of the ions in a smooth jellium model up to first-order perturbation in the pseudopotential. In contrast to the good results obtained for the crystalline metal surfaces, the resulting surface tension for the liquids was too high compared with the experiment. These authors concluded that inclusion of the second-order terms (screening effects) is of crucial importance.

Hasegawa and Watabe[8] (hereafter HW) carried out a rigorous second-order perturbation theory for the surface tension. Such a formulation improved the results for the surface tension. However, it gave an arbitrarily small ionic profile width, a feature that is clearly unphysical. Chacón, Flores, and Navascués[9] (hereafter CFN) improved, the method adopting a more realistic electronic reference system including an external potential. This reference system reflects the average over the ionic configurations of the charge induced by the pseudopotential. In this way, although the induced charge may be important for a given ionic configuration, the average over all ionic configuration is zero. The main advantage of this electronic reference system is that it makes the theory less sensitive to changes in the pseudopotential and to the approximation used for the surface electronic response function. Lai,[11] using a similar approach, calculated the surface tension with a full nonlocal pseudopotential. He found that using the HW electron reference system yielded surface tensions of liquid metals, which are much smaller than the results of the local calculations. However, with the CFN electron reference system he obtained values close to the local ones, although the predicted surface profile widths were still unrealistically small. The CFN theory, neglecting the electrostatic energy, justifies from a microscopic point of view the pseudoatom model where a locally vanishing induced charge is assumed.[9,10]

The failure of these previous theories in predicting reasonable values for the ionic profile width could be due to two reasons: the use of monotonic functions to describe the density profile and the approximation used for the surface electronic response. Foiles and Ashcroft,[12] using the electronic reference system of HW, studied the dependence of the surface tension on the surface screening. When they, in the calculation of the self-energy, made an approximation on the effective pair potential similar to that of Evans and Kumaravadiviel [see Eq. (1)], they obtained negative values for the surface tension of the polyvalent metals. They concluded that it is essential to include the self-energies correctly, and therefore very accurate values of the response function of the inhomogeneous electron gas are required. We think that the negative surface tensions obtained by them are corrected when the CFN reference system is used, and that the overestimation of the self-energy due to the approximate response function could be counteracted in part by the underestimation of the energy due to the pair interaction. In any case, this is an open question that we will study in future work.

The purpose of this paper is to study the other question, i.e., the effect of nonmonotonic density profiles on the surface tension. The only theoretical results with a nonmonotonic ionic density profile, and within the second-order approximation, are due to Hasegawa.[13] This author introduced a classical one-component plasma (OCP) as an ionic reference system for the variational calculation instead of a hard-sphere fluid that had been used in almost all previous studies. The OCP choice has two problems; the first one is that the OCP is less well understood than the hard sphere system and, at the moment, there is no available theory that satisfactorily describes the inhomogeneous OCP. The density gradient expansion used by Hasegawa is quite sensitive to the coefficient of the square of the gradient. The value of this coefficient is only well known in the weak-coupling regime and the gradient expansion has not yet been tested in other regimes. The second problem is that the method consists in replacing the internal energy, due to the effective pair interaction between ions, by the excess internal energy of an OCP with a density-dependent effective-coupling constant. A similar idea is used for the excess part of the entropy. This approximation, which was developed for a homogeneous system, was extended to the surface problem by Hasegawa who used a local treatment of the effective-coupling constant. However, it is not clear what influence this approximation has on the results. For alkali metals he obtained values for the surface tension that are close to the experimental ones, but for polyvalent metals poor results were obtained.

Extensive Monte-Carlo simulations of the liquid-vapor density profile have been carried out by Rice and coworkers.[14] The Hamiltonian belongs to the pseudoatom model type, and they use a second-order perturbation method to calculate the effective potential between ions. As they cannot obtain values for the surface tension, they only study the surface structure. The resulting ion-density profiles exhibit large and slowly decaying oscillations. The x-ray reflectance experiments[15] on liquid metals also support the existence of such stratified structures, although the analysis of the experimental data is not unique.

Altogether, the problem of the liquid-vapor interface structure of simple liquid metals is an open question. In this work we improve the CFN theory in order to develop a model capable of describing the surface tension and the shape of the ionic profile. This model using the hard-sphere fluid as reference system for the ions. The paper is arranged as follows. In Sec. II we review the general theory of non-uniform liquid metals. The main difference between this model and the CFN theory is presented in the Sec. III, where we write down the different contributions to the surface tension. In the Sec. IV we discuss our numerical results and compare them with previous results and experimental information. Finally we present our conclusions.

II. PSEUDOPOTENTIAL PERTURBATION THEORY FOR NONUNIFORM LIQUID METALS

Following CFN, we consider a simple inhomogeneous metal of N ions of valence Z and NZ valence electrons at temperature T. For simplicity we assume that the electron-ion interactions are described by a local pseudopotential $v_{\mathrm{ps}}(|\mathbf{r}|)$. The total Hamiltonian of the system (using atomic units throughout this paper, $\hbar = m = e = 1$) is written as

$$H = \sum_{l} \frac{P_l^2}{2M} + \sum_{l<m} \frac{Z^2}{|\mathbf{R}_l - \mathbf{R}_m|} + \sum_{i,l} v_{\mathrm{ps}}(|\mathbf{r}_i - \mathbf{R}_l|) + \sum_{i} \frac{p_i^2}{2} + \sum_{i<j} \frac{2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (2)$$

where $\mathbf{r}$ and $\mathbf{p}$ are the electronic position and momentum operators, and the corresponding quantities for ions are $\mathbf{R}$ and $\mathbf{P}$. It is usual to split the total Hamiltonian into ionic (H_{ii}), electronic (H_{ee}), and electron-ion (H_{ei}) interaction parts. A compensating background is added and subtracted in order to avoid the well-known problems arising from the long-range Coulomb interactions in the thermodynamic limit. This can be done in several ways; we shall follow the CFN steps and write

$$\begin{aligned} H_{ii} &= \sum_l \frac{P_l^2}{2M} + \sum_{l<m} \frac{Z^2}{|\mathbf{R}_l - \mathbf{R}_m|} - \frac{Z^2}{2} \int d\mathbf{R} \int d\mathbf{R}' \frac{\rho(\mathbf{R})\rho(\mathbf{R}')}{|\mathbf{R}-\mathbf{R}'|} = U_K + U_M, \\ H_{ee} &= \sum_i \frac{p_i^2}{2} + \sum_{i<j} \frac{2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{Z^2}{2} \int d\mathbf{R} \int d\mathbf{R}' \frac{\rho(\mathbf{R})\rho(\mathbf{R}')}{|\mathbf{R}-\mathbf{R}'|} + V_{\text{ext}}(\mathbf{r}), \\ H_{ei} &= \sum_{i,l} v_{\text{ps}}(|\mathbf{r}_i - \mathbf{R}_l|) - \sum_i V_{\text{ext}}(\mathbf{r}_i), \end{aligned} \tag{3}$$

where

$$V_{\text{ext}}(\mathbf{r}) = \int d\mathbf{R} \rho(\mathbf{R}) v_{\text{ps}}(|\mathbf{r} - \mathbf{R}|). \tag{4}$$

U_M and U_K are the Madelung and kinetic terms of H_{ii}, and $\rho(\mathbf{r})$ is the average ion density. As shown in CFN, with this choice for the Hamiltonian splitting we are using an electron reference system that collects the average of the pseudopotential-induced charge $\delta n(\mathbf{r})$ of each ionic configuration. In other words, although $\delta n(\mathbf{r})$ may be important for a given ionic configuration, its average over all ionic configurations $\langle \delta n(\mathbf{r}) \rangle$ is zero. This approach has several consequences. One of them is that the average of the electron density over all the ionic configurations is equal to the electron density of the reference system. A second one is that U_1 and $U_{2,nc}$, which are present in the HW formalism, are identically zero in our model. For a more careful discussion of this topic see Ref. 9.

To proceed, we apply the Born-Oppenheimer adiabatic approximation to reduce the two-component nature of the liquid metal to a one-component system. It consists of classical ions described by an effective Hamiltonian,

$$H_{\text{eff}} = H_{ii} + F_{\text{el}} + \frac{Z^2}{2} \int d\mathbf{R} \int d\mathbf{R}' \frac{\rho(\mathbf{R})\rho(\mathbf{R}')}{|\mathbf{R}-\mathbf{R}'|} \tag{5}$$

with

$$\begin{aligned} F_{\text{el}} &= -\beta^{-1} \ln \text{Tr}_{\text{el}} \exp[-\beta(H_{\text{el}} + H_{ei})] \\ &\quad - \frac{Z^2}{2} \int d\mathbf{R} \int d\mathbf{R}' \frac{\rho(\mathbf{R})\rho(\mathbf{R}')}{|\mathbf{R}-\mathbf{R}'|}. \end{aligned} \tag{6}$$

Using the density-functional formalism of Hohenberg and Kohn,[16] the electronic Helmholtz free energy (F_{el}) for a fixed ionic configuration can be expressed as

$$F_{\text{el}} = F_{\text{el}}^0[n(\mathbf{r})] + \int d\mathbf{r} n(\mathbf{r}) \Delta v_{\text{ps}}(\mathbf{r}), \tag{7}$$

with

$$\Delta v_{\text{ps}}(\mathbf{r}) = \sum_l v_{\text{ps}}(\mathbf{r} - \mathbf{R}_l) - V_{\text{ext}}(\mathbf{r}). \tag{8}$$

F_{el}^0 is the Helmholtz free energy of the electron gas-reference system [i.e., an electron gas in a external potential $V_{\text{ext}}(\mathbf{r})$]. We now choose $n_0(\mathbf{r})$ to be the equilibrium electron density of the unperturbed system F_{el}^0, and evaluate F_{el} using a second-order perturbation treatment of $\Delta v_{\text{ps}}(\mathbf{r})$. This approach gives

$$F_{\text{el}} = F_{\text{el}}^0 + U_1 + U_2, \tag{9}$$

where

$$F_{\text{el}}^0 = \Im[n_0(\mathbf{r})] + \int d\mathbf{r} n_0(\mathbf{r}) V_{\text{ext}}(\mathbf{r}). \tag{10}$$

$\Im[n_0(\mathbf{r})]$ is the intrinsic free energy of the electrons. The first (U_1) and second (U_2) order terms due to v_{ps} are equal to

$$U_1 = \int d\mathbf{r} n_0(\mathbf{r}) \Delta v_{\text{ps}}(\mathbf{r}), \tag{11}$$

$$U_2 = \int d\mathbf{r} \delta n_0(\mathbf{r}) \Delta v_{\text{ps}}(\mathbf{r}). \tag{12}$$

The induced charge density $\delta n_0(\mathbf{r})$ for a given ionic configuration is determined using linear response theory:

$$\delta n(\mathbf{r}) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}') \Delta v_{\text{ps}}(\mathbf{r}'). \tag{13}$$

$\chi(\mathbf{r}, \mathbf{r}')$ being the response function of the electron gas reference system. With this result, the effective Hamiltonian takes the form

$$\begin{aligned} H_{\text{eff}} &= H_{ii} + F_{\text{el}}^0 + \frac{Z^2}{2} \int d\mathbf{R} \int d\mathbf{R}' \frac{\rho(\mathbf{R})\rho(\mathbf{R}')}{|\mathbf{R}-\mathbf{R}'|} \\ &\quad + U_1 + U_2. \end{aligned} \tag{14}$$

Using the Gibbs-Bogoliubov inequality,[17] it can be shown that the Helmholtz free energy of a system described by a Hamiltonian H_{eff} has an upper limit given by

$$F = F_{\text{ref}} + \langle H_{\text{eff}} - H_{\text{ref}} \rangle_{\text{ref}}, \tag{15}$$

where H_{ref} and F_{ref} are the Hamiltonian and free energy of a reference system. The bracket in this equation represents a thermal average over the reference system. With the choice of the external potential given by Eq. (4), it is obvious that $\langle \delta n(\mathbf{r}) \rangle = 0$ because $\langle \Delta v_{\text{ps}}(\mathbf{r}) \rangle = 0$. In the same way, the term $\langle U_1 \rangle$ and the contribution to $\langle U_2 \rangle$, given by

$$U_{2,nc} = \int d\mathbf{r} \langle \Delta v_{\text{ps}}(\mathbf{r}) \rangle \langle \delta n(\mathbf{r}) \rangle. \tag{16}$$

are also neglected. We have selected a system of hard spheres to be our reference system for the ions. Hasegawa and Watabe[13] commented that this reference system is not very useful for a surface problem because it does not form a free surface; to avoid such a problem we have to introduce an artificial external field to confine the particles inside the surface. We think that in order to apply the Gibbs-Bogoulibov inequality we only need to know the free energy of the hard-sphere system with density $\rho(\mathbf{r})$, even if this profile were not an equilibrium profile. We shall later present a procedure to calculate this Helmholtz free energy without needing to introduce an external field.

With the choice of a hard-sphere fluid as the reference system we find finally

$$F < F_{\rm hs} + F^0_{\rm el} + U_{\rm eff} + U_{\rm self}\,, \tag{17}$$

where

$$U_{\rm eff} = \int d\mathbf{R} \int d\mathbf{R}' \rho(\mathbf{R})\rho(\mathbf{R}')\phi_{\rm eff}(\mathbf{R},\mathbf{R}')[g_{\rm hs}(\mathbf{R},\mathbf{R}')-1], \tag{18}$$

being

$$\begin{aligned}\phi_{\rm eff}(\mathbf{R},\mathbf{R}') &= \frac{Z^2}{|\mathbf{R}-\mathbf{R}'|} + \phi_{\rm ind}(\mathbf{R},\mathbf{R}'),\\ \phi_{\rm ind}(\mathbf{R},\mathbf{R}') &= \int d\mathbf{r} \int d\mathbf{r}' v_{\rm ps}(|\mathbf{r}-\mathbf{R}|)\\ &\quad \times \chi_0(\mathbf{r},\mathbf{r}')v_{\rm ps}(|\mathbf{r}'-\mathbf{R}'|),\end{aligned} \tag{19}$$

and

$$\begin{aligned}U_{\rm self} &= \tfrac{1}{2}\int d\mathbf{R}\phi_{\rm self}(\mathbf{R})\rho(\mathbf{R}),\\ \phi_{\rm self}(\mathbf{R}) &= \phi_{\rm ind}(\mathbf{R},\mathbf{R}).\end{aligned} \tag{20}$$

It is worth noting that the $U_{\rm eff}$ term is obtained by rearranging the Madelung and pair-interaction energy terms in CFN.

III. APPLICATION TO LIQUID-METAL SURFACES: THE SURFACE TENSION

In this section we derive an expression for the surface tension of a planar liquid-metal surface. We can identify the surface tension with the surface excess of Helmholtz free energy per unit area, provided we locate the Gibbs dividing surface at the zero adsorption plane. In this case, and in accordance with the definition of excess Helmholtz free energy, we obtain

$$\sigma = \frac{1}{2A}(2F - F^{\rm bulk}), \tag{21}$$

where A is the area of the planar surface and $F^{\rm bulk}$ the bulk-liquid Helmholtz free energy. The main differences between the present theory and the previous CFN are (a) the free energy for a nonhomogeneous hard spheres fluid is obtained in the weighted density approximation[18] instead of in the Kirkwood-Buff scheme, (b) we study the electron reference system using an explicit nonlocal kinetic energy functional developed by Chacón *et al.*[23] instead of the gradient expansion approximation (also, we do not need to parametrize the electronic profile because we use a conjugate gradient method in order to minimize the free energy functional) and (c) the surface effective-pair potential is parametrized instead of the Taylor expansion used previously. We shall now give the contributions to the surface tension, paying special attention to showing these differences.

A. Hard-sphere reference system

Instead of the Kirkwood-Buff[17] scheme used previously by other authors, we have approximated the exact expression of the free-energy functional for a nonhomogenous hard-sphere fluid by the weighted density approximation.[18] This is a nonlocal density functional, which preserves the simplicity of a local-density approximation but remains physically sensible when the density exhibits significant oscillations over molecular length scales. In this theory, the free energy is written as

$$F_{\rm hs}[\rho] = F_{\rm ideal}[\rho] + \int d\mathbf{r}\rho(\mathbf{r})\psi_{\rm ex}(\bar\rho(\mathbf{r})), \tag{22}$$

where $F_{\rm ideal}$ is the Helmholtz free energy of a noninteracting system and $\psi_{\rm ex}(\rho) = [f_{\rm hs}(\rho) - f_{\rm ideal}(\rho)]/\rho$ is the excess hard sphere free energy per atom in a uniform system. For $f_{\rm hs}$ we have used the Carnahan and Starling[19] equation of state. Several versions of the WDA exist, each one corresponding to different recipes for determining the value of the average density $\bar\rho(\mathbf{r})$. In this paper we follow Tarazona's procedure,[20] where the average density is determined by the implicit equation

$$\bar\rho(\mathbf{r}) = \int d\mathbf{r}'\theta(|\mathbf{r}-\mathbf{r}'|;\bar\rho(\mathbf{r}))\rho(\mathbf{r}'). \tag{23}$$

The weight function θ is specified by requiring that (22) and (23) produce, upon double functional differentiation, a direct correlation function $c^2(\rho;r)$ close to the corresponding Percus-Yevick result. This weight function has to be normalized in order to recover the bulk free energy value in the homogeneous limit. The explicit equation for θ is given in Ref. 20. The surface tension is equal to

$$\begin{aligned}\sigma_{\rm hs} &= \int_{-\infty}^{\infty} dz\rho(z)[f_{\rm ideal}(\rho(z)) - f_{\rm ideal}(\rho_B)]\\ &\quad + \int_{-\infty}^{\infty} dz\rho(z)[\psi_{\rm ex}(\rho(z)) - \psi_{ex}(\rho_B)]dz,\end{aligned} \tag{24}$$

where we have taken the z axis perpendicular to the surface. Tarazona[20] compared the results of this theory, applied to the density profile and surface tension of hard spheres against a hard wall, with computer simulation and with the Kirkwood-Buff formulas using the superposition approximation. The agreement with the simulation results is better than that of the Kirkwood-Buff theory, reducing the incorrect large ionic oscillations of this last theory, specially at high bulk density. He finds that this functional not only gives the correct value for the free energy at the minimum, but also the right position of the minimum of the grand potential energy in the density functional space. This last feature is very important, since in this work we are interested in the possible density profile oscillations.

B. Electron reference system

Our electron reference system is a jellium metal surface with a positive charge background $Z\rho(\mathbf{r})$ in equilibrium with an external field $V_{\rm ext}(\mathbf{r})$. Hohenberg and Kohn[16] proved the existence of an energy-density functional for the ground-state energy of an interacting inhomogeneous electron gas, which reaches its minimum value at the ground-state density distribution. The minimum value of the functional gives the ground-state energy. Since the electrons in liquids metals are still degenerate near the melting point, we can approximate their free energy with the ground-state energy and obtain

$$F_{\mathrm{el}}^0 = T[n] + E_{\mathrm{xc}}[n] + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\frac{[n(\mathbf{r}) - Z\rho(\mathbf{r})][n(\mathbf{r}') - Z\rho(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r} n(\mathbf{r})\left(V_{\mathrm{ext}}(\mathbf{r}) + Z\int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\right). \tag{25}$$

$T[n]$ is the kinetic energy term, which would be the full energy of a noninteracting electron system. $E_{\mathrm{xc}}[n]$ is the exchange and correlation energy. The third term in (26) is the electrostatic energy, and the last term is due to the external potential; it is formally equal to the first-order term of Hasegawa and Watabe.[8] For the exchange and correlation energy we use the simplest approximation, the local density:

$$E_{\mathrm{xc}} = \int d\mathbf{r} n(\mathbf{r})\epsilon_{\mathrm{xc}}(n(\mathbf{r})), \tag{26}$$

where ϵ_{xc} is the exchange and correlation energy per electron in a uniform bulk phase at density $n(\mathbf{r})$. We have used the Nozières-Pines interpolation formula for ϵ_{xc}. The last term in (26) is equal to

$$\int d\mathbf{r} n(\mathbf{r})\int d\mathbf{R}\rho(\mathbf{R})\omega(|\mathbf{r}-\mathbf{R}|), \tag{27}$$

where $\omega(r) = v_{\mathrm{ps}}(r) + Z/r$ is the so-called repulsive part of the pseudopotential. Aschroft's[21] empty-core model is used for the pseudopotential

$$v_{\mathrm{ps}}(\mathbf{r}) = \begin{cases} 0 & \text{for } r < r_c \\ -Z/r & \text{for } r \geq r_c . \end{cases} \tag{28}$$

$T[n]$ could be calculated exactly solving the Lang and Kohn problem, but this is a computationally time consuming process, and we prefer to use an approximate functional. We choose an explicit nonlocal functional of the electron density developed by Chacón *et al.*,[23] which is formally similar to the one used for the hard-sphere reference system. This density functional is constructed to give the exact energy and the linear response function in the homogeneous limit. The kinetic functional is written as

$$T[n] = \frac{8}{5}\int d\mathbf{r} n(\mathbf{r})t(\bar{n}(\mathbf{r})) - \frac{3}{5}\int d\mathbf{r} n(\mathbf{r})t(n(\mathbf{r})) + \frac{1}{4}\int d\mathbf{r}\frac{|\nabla n(\mathbf{r})|^2}{n(\mathbf{r})}, \tag{29}$$

where $t(n)$ is the mean kinetic energy per electron in a uniform phase and the average density $\bar{n}(\mathbf{r})$ is given by

$$\bar{n}(\mathbf{r}) = \int d\mathbf{r}'\tau(|\mathbf{r}-\mathbf{r}'|; n(\mathbf{r}))n(\mathbf{r}'), \tag{30}$$

τ being a normalized weight function. τ is determined by the condition that the second functional derivative of $T[n]$ at uniform density $n(\mathbf{r}) = n_B$ be equal to the reciprocal of the Lindhard susceptibility. An explicit expression for τ is given in Ref. 23.

In the same way as in CFN, we minimize, for a given ionic profile, the jellium surface tension defined by

$$\sigma_{\mathrm{jell}} = \frac{1}{2A}(2F_{\mathrm{el}} - F_{\mathrm{el}}^{\mathrm{bulk}}), \tag{31}$$

and then we find the minimum value of the surface tension by varying the ionic profile. All previous studies of liquid metals with an approximate functional for $T[n]$ were variational calculations, and the minimization of $F[n]$ was restricted to a family of density profiles. The simplest and most usual parametrization is the exponential profile with a single parameter to vary the interface width. This procedure is not very useful in our case because we are especially interested in the study of the surface-density oscillations. In this work, we use the conjugate gradient method, modified by Tarazona and Chacón,[24] in order to obtain the numerical exact electronic profile which minimizes the free-energy functional. Using this method, Tarazona and Chacón[24] studied the jellium surface and have shown that Eq. (29) seems to be the best existing form for an explicit functional $T[n]$. The electronic profiles show a first maximum of $n(z)$ with a height and position in excellent agreement with the exact Lang and Kohn results.[1] They also get the oscillating tail, which is missing in the gradient expansion approximation.

C. Madelung and second-order terms

In order to make further progress, it is necessary to know the surface radial distribution function $g_{\mathrm{hs}}(\mathbf{R},\mathbf{R}')$ and the surface electronic response function $\chi(\mathbf{r},\mathbf{r}')$. Without any reliable theory to calculate both quantities, it is necessary to use some simplifications. We approximate $g_{\mathrm{hs}}(\mathbf{R},\mathbf{R}')$ with the radial distribution function of the bulk liquid, i.e.,

$$g_{\mathrm{hs}}(\mathbf{R},\mathbf{R}') = g_{\mathrm{hs}}(|\mathbf{R}-\mathbf{R}'|;\rho_B). \tag{32}$$

This approximation has been shown to be quite reasonable for simple liquids.[25] However, the use of this approximation in systems interacting via the long-range Coulomb potential leads to serious problems.[26] Fortunately, the Coulomb interaction is strongly screened by the electrons in our case. This means that $\phi_{\mathrm{eff}}(\mathbf{r})$ is shorter ranged than the Coulomb potential, and the use of the approximation is reasonable.

Following Hasegawa and Watabe, we prefer to make an approximation on $\phi_{\mathrm{ind}}(\mathbf{R},\mathbf{R}')$, instead of making a direct approximation for $\chi(\mathbf{r},\mathbf{r}')$. We have considered two approximations. In the first one (approximation A) we replace the exact $\phi_{\mathrm{ind}}(\mathbf{R},\mathbf{R}')$ by that calculated for the bulk-liquid metal, i.e.,

$$\begin{gathered} \phi_{\mathrm{ind}}(\mathbf{R},\mathbf{R}') = \phi_{\mathrm{ind}}(|\mathbf{R}-\mathbf{R}'|;\rho_{\mathrm{ind}}), \\ \phi_{\mathrm{self}}(\mathbf{R}) = \phi_{\mathrm{self}}(R;\rho_{\mathrm{self}}), \end{gathered} \tag{33}$$

where

$$\rho_{\mathrm{ind}} = \rho_{\mathrm{self}} = \rho_B . \tag{34}$$

This approximation is equivalent to using the bulk value for the surface response function. In the second one (approximation B) we make $\phi_{\rm ind}(\mathbf{R},\mathbf{R}')$ equal to that calculated for a homogeneous liquid metal with a density equal to the average of the local electron densities at the ion positions $\mathbf{R}$ and $\mathbf{R}'$, i.e., substitute

$$\rho_{\rm ind} = \frac{\rho(\mathbf{R}) + \rho(\mathbf{R}')}{2}, \qquad \rho_{\rm self} = \rho(\mathbf{R}), \tag{35}$$

into Eqs. (33). Using these approximations we can write the contribution from $\sigma_{\rm eff}$ and $\sigma_{\rm self}$ to the surface tension as

$$\begin{aligned}\sigma_{\rm eff} = \pi \int_{-\infty}^{\infty} dZ_R\,\rho(Z_R) \int_{-\infty}^{\infty} dZ_T \\ [\rho(Z_R + Z_T)\Phi(Z_T;\rho_{\rm ind}) - \rho_B\Phi(Z_T;\rho_B)],\end{aligned} \tag{36}$$

$$\sigma_{\rm self} = \int_{-\infty}^{\infty} dZ\,\rho(Z)[\phi_{\rm self}(\rho_{\rm self}) - \phi_{\rm self}(\rho_B)],$$

where

$$\Phi(Z_T;\rho_{\rm ind}) = \int_{|Z_T|}^{\infty} dT\; T\; \phi_{\rm eff}(T;\rho_{\rm ind})\;[g_{\rm hs}(T;\rho_B) - 1]. \tag{37}$$

In approximation A the self-screening term does not contribute to the surface tension and the calculation of $\sigma_{\rm eff}$ is the same as in HW and CFN.[8,9] In approximation B the exact evaluation of term (36) was difficult.[8,9] In order to make things simpler, HW and CFN expanded $\phi_{\rm ind}(\mathbf{R},\mathbf{R}')$ around either ρ_B or $\rho_B/2$ retaining only the lowest-order terms. We have evaluated $\sigma_{\rm eff}$ by parametrizing the function $\Phi(z,\rho)$. In this parametrization the range of the variable z is split in sectors in which the function $\Phi(z,\rho)$ is fitted to a polynomial. Note that the size of the sectors and the degree of the polynomials in each sector could be different. Finally the dependence with the density of each coefficient is fitted to another polynomial in density. In that way we obtain

$$\Phi(z,\rho) = \sum_{i=1}^{n} H(z - z_i)H(z_{i+1} - z) \times \sum_{j=0}^{j_M(i)} (z - z_i)^j \sum_{k=0}^{K_M(i,j)} A_{ij}^k \rho^k, \tag{38}$$

where the values of z_i are the extrema of each sector and H is the Heaviside function. With this parametrization and using a parametrized ionic profile, it is possible to evaluate some integrals analytically.

IV. NUMERICAL RESULTS AND DISCUSSION.

The values of the bulk parameters used in this work are given in Table I. The radius for the pseudopotential empty cores is taken from Cohen and Heine,[22] although for the Cs we have used a different one, fitted to obtain a hard-sphere packing fraction close to 0.45. The static bulk electronic response function employed is that proposed by Geldart and Vosko,[27] which verifies the compressibility sum rule when using our exchange and correlation energy density. For the bulk radial hard-sphere distribution function we use the Percus-Yevick approximation.[17,28] The hard-sphere diameter has been determined by minimizing the bulk Helmholtz free energy when the density equals the experimental density.

TABLE I. Values of the experimental electron density (n_B), pseudopotential core radius (r_c), and hard-sphere diameter ($d_{\rm hs}$) used in this work for several metals at the melting temperature (T).

Metal	T(K)	n_B (a.u)	r_c (a.u.)	$d_{\rm hs}$ (a.u)
Cs	301	1.23×10^{-3}	2.62	8.81
K	337	1.89×10^{-3}	2.12	7.51
Na	371	3.59×10^{-3}	1.70	6.12
Mg	924	11.67×10^{-3}	1.39	5.39
Al	933	23.61×10^{-3}	1.12	4.85

Once the bulk parameters are fixed, the ionic profile is the only quantity to be determined by the minimum condition of the total surface tension:

$$\sigma = \sigma_{\rm hs} + \sigma_{\rm jell} + \sigma_{\rm eff} + \sigma_{\rm self}, \tag{39}$$

since the electronic profile is obtained, for each ionic profile, by minimizing $\sigma_{\rm jell}$. In this work we do not need to parametrize the electronic density because the conjugate gradient method used in the minimization of $\sigma_{\rm jell}$ gives the exact (numerical) solution for the electronic profile.

Before presenting the results obtained for nonmonotonic ionic density profiles, we check the theory developed in this work by using exponential profiles, since it is the parametrization commonly used for previous theories. In this case, we calculate the surface tension selecting a density profile of the form

$$\rho(z) = \begin{cases} \rho_B[1 - \frac{1}{2}\exp(z/M)], & z < 0 \\ \frac{\rho_B}{2}\exp(-z/M), & z \geq 0, \end{cases} \tag{40}$$

where we have set the density of vapor equal to zero. The results are given in Table II. Note that the results using CFN are different to those presented in the original article because there they used the Madelung energy misprinted in the original article by Jones.[29] We have corrected that and have recalculated the CFN (hereafter C-CFN) values for the surface tension σ, as given in the Table II. The main differences with respect to the original CFN results are small changes in the surface tension and, more importantly, the ionic profile in approximation B is now a step function instead of the narrow profile obtained previously. In addition, we have calculated, with the C-CFN theory, the temperature derivative of the surface tension $(\partial\sigma/\partial T)_P$ using the experimental values of the coefficient of thermal expansion. The results obtained, which are presented in Table III, agree reasonably with the experimental values. For alkali metals our values are similar to those obtained by Hasegawa[13] using an OCP as the reference system for the ionic component,

TABLE II. Calculated surface tension σ and its components parts (all is in units of erg cm^{-2}) using an exponential profile. The table includes the ionic profile parameter M. A and B refer to the approximation schemes described in the text. The experimental results were taken from Allen. ** means that the minimization procedure does not converge.

Metal	Approx.	M	σ_{jell}	σ_{hs}	σ_{eff}	σ_{self}	σ	σ^{a}	M^{b}	σ^{b}	σ^{expt}
Cs	A	0.206	−27	−15.5	127.2	0.0	84.7	54	0.59	74.83	70
	B	0.118	−26	−15.2	117.2	19.7	95.7	68			
K	A	0.334	−40.9	−20.9	171	0.0	110	87	0.493	107.7	115
	B	0.127	−34.4	−19.7	153	28.6	128	104			
Na	A	0.565	−170	−44.6	380	0.0	165.8	138	0.568	165.8	191
	B	0.119	−114.3	−38	310.6	57	215	170	0.003	204.2	
Mg	A	0.196	−1487	−170	2028	0.0	371	153	* *	* *	559
	B	0.057	−1519	−163	1870	547.8	735	456	0.004	655.7	
Al	A	0.801	−7374	−273	7795	0.0	147	15	* *	* *	1050
	B	0.0	−4348	−188	4293	1745	1502	960	0.0	1366.8	

[a] Reference 8.
[b] Reference 9 (corrected).

but our results show an improvement over his for polyvalent metals. This result shows that use of the hard-sphere fluid as ionic reference system gives a good description of $(\partial\sigma/\partial T)_P$.

We now will discuss approximation A for the present theory. Contrary to previous theories, except the C-CFN, the predicted ion density is not a step function. In any case the width of the surface region is very small. The surface tensions for all metals are smaller than the experimental values, the difference being bigger for the polyvalent metals. If we compare these results with the C-CFN, we must emphasize that for polyvalent metals C-CFN yields negative values for the surface tension and the minimization procedure does not converge. The reason is that the minimization procedure is very sensitive to including the first-order perturbation term in the electronic reference system. In the C-CFN case the gradient expansion used for $T[n]$ does not give enough accuracy to avoid the aforementioned misbehavior. On the other hand, HW used the same gradient expansion, always obtaining a solution, since they use another electronic reference system. In this case the procedure is less sensitive to the approximation used in $T[n]$. We get a narrow profile instead of the step function obtained by HW,[8] due to the different approximation used for the F_{hs}. As noted by CFN,[9] the value of the surface tension show little sensitivity to the approximation for F_{hs}, but an accurate determination of the ionic profile requires a very good description for F_{hs}.

TABLE III. Temperature derivative of the surface tension $(d\sigma/dT)_p$, calculated using C-CFN (erg cm^{-2}K^{-1}). The experimental results were taken from Allen.

Metal	$(d\sigma/dT)_p$	$(d\sigma/dT)_p{}^{\text{a}}$	$(d\sigma/dT)_p^{\text{expt}}$
Cs	−0.05	−0.055	−0.06
K	−0.05	−0.067	−0.08
Na	−0.09	−0.114	−0.09
Mg	−0.33	−0.257	−0.35
Al	−0.27		−0.35

[a] Reference 8.

Approximation B predicts a small profile width for the alkali metals, whereas the ionic profile is almost a step function for the polyvalent metals. The surface tension for all metals are in better agreement with the experimental values than those obtained with approximation A. The changes due to the improvement on the calculation of $\Phi(z,\rho)$ are smaller than we would expect; this could be due to the exponential parametrization of the ionic profile. Figures 1(a) and 2(a) show the ionic and electronic profiles, within approximation B, for the sodium and aluminum, respectively.

From now on we will only use approximation B, since it gives much better values for the surface tension than approximation A. The first parametrized profile that we have chosen for the study of oscillations near the liquid-metallic surface is given by

$$\rho(z)=\begin{cases}\rho_B[1-B\exp(z/M_1)\cos(\beta z)], & z<0\\ \rho_B(1-B)\exp(-z/M_2), & z\geq 0.\end{cases} \tag{41}$$

The two parameters are fixed by the requirements that $\partial\rho(z)/\partial z$ be continuous at z=0 and that the Gibbs dividing surface must be located at z=0. We have chosen this parametrization because it is the same one used by Hasegawa[13] in the study of the liquid-metal surface using OCP as an ionic reference system. The results for the surface tension are shown in Table IV. For all simple metals, except cesium, our results for the surface tension are in a good agreement with experiment. It is worthwhile to remark that the surface tension slightly decreases with respect to the values obtained with the exponential profile. If we compare with Hasegawa's results,[13] we see that the results are similar for the alkali metals, but in the case of polyvalent metals our theory is better, since his theory is only applicable to magnesium and the value obtained is much higher than experimental value.

Figures 1(b) and 2(b) show our results for the density profiles for sodium and aluminum using the ionic profile parametrization given by (41). For both metals we obtain profiles with quite pronounced oscillations, and the height of the first peak for the sodium is slightly larger than the Hasegawa[13] results. On the other hand, the height of the first peak for aluminum is larger than that for sodium. This is an amazing result. We think it is due to the pathologic parametrization (41) of the ionic profile. This parametrization only has two free parameters, having linked all the different parameters, and so it is not very flexible. We think that is the reason for the small changes in the surface tension values with respect to those obtained with the exponential profile.

In order to check if this conjecture is correct, we have tried another ionic profile parametrization:

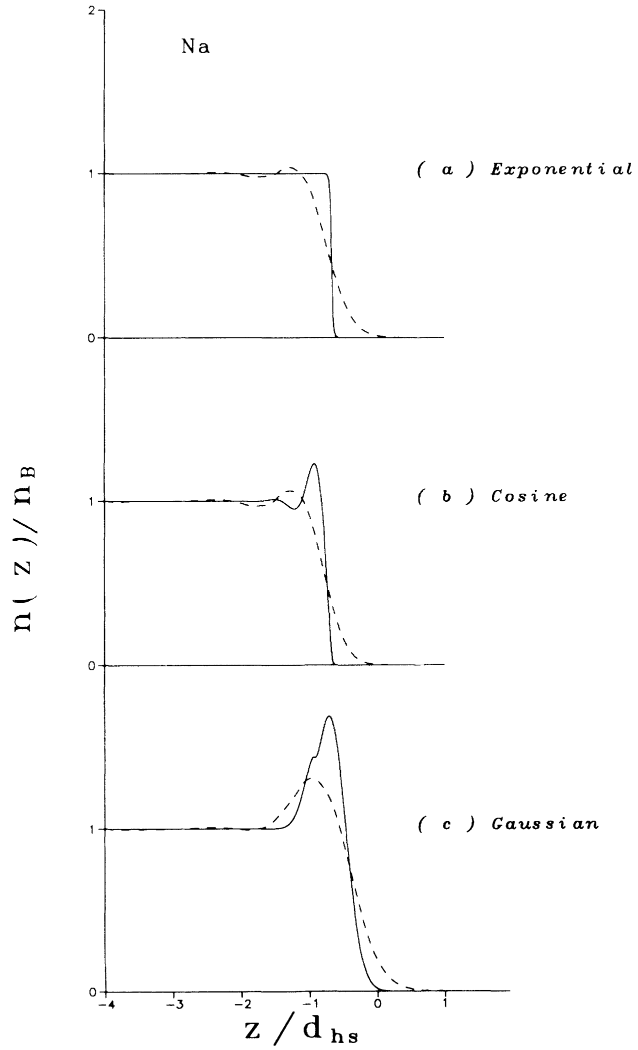

FIG. 1. Results of variational calculations in our theory for the surface density profiles of the sodium; full line is ionic profile and dashed line is the electronic profile. (a) Exponential parametrization, (b) cosine parametrization, and (c) Gaussian parametrizaton.

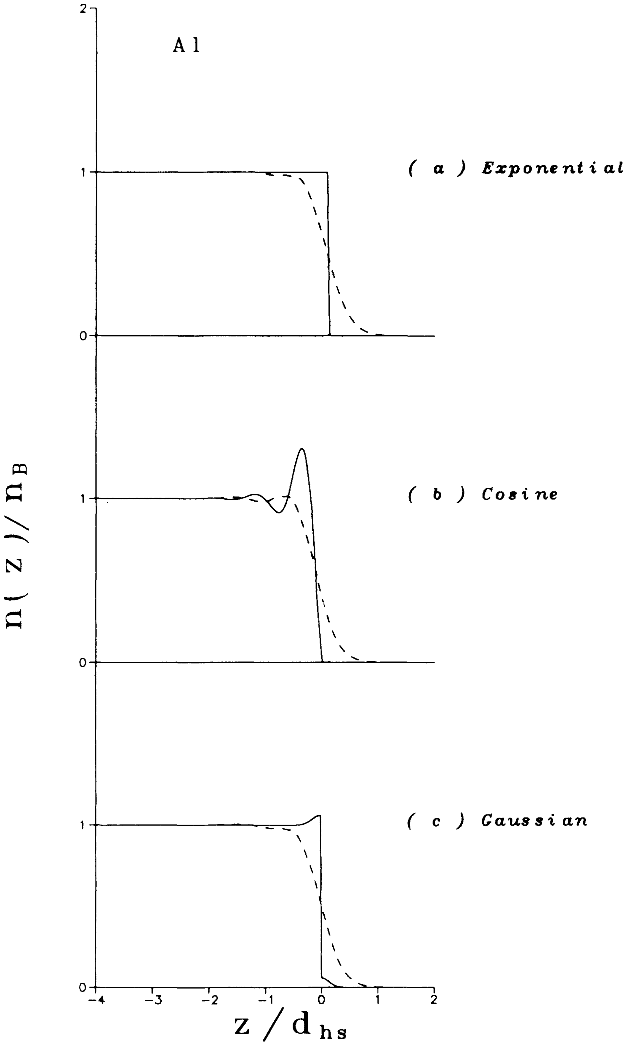

FIG. 2. Same as Fig. 1 for aluminum.

TABLE IV. Calculated surface tension σ and its components parts within of the approximation B and using a nomonotonic ionic profile. Cosine and Gaussian refer to the parametrization (41) and (42), respectively, described in the text (all units are erg cm^{-2}).

Metal	Profile	σ_{jell}	σ_{hs}	σ_{eff}	σ_{self}	σ	σ^{a}	σ^{expt}
Cs	Cosine	−15.4	−14.3	105	18	93.7	69	70
	Gaussian	228	32	−182	−20	57.4		
K	Cosine	−15.1	−18.7	138.3	22	126.8	111	115
	Gaussian	616.7	99	−594.5	−66	55.25		
Na	Cosine	−57.82	−33.9	249.3	46.4	203.9	215	191
	Gaussian	756.9	104.6	−685.6	−65.8	110		
Mg	Cosine	−874.4	−138.3	1306.4	400.6	689.2	873	559
	Gaussian	−901.7	−2.2	−556.7	114.6	457		
Al	Cosine	−2455.6	−154.7	2473	1339	1202		1050
	Gaussian	−4476	−191	4150	1658	1147		

[a] Reference 13.

$$\rho(z)=\begin{cases}\rho_B\left\{1-C\exp(z/M)\right. \\ \qquad\left.+A_1\exp\left[\left(\dfrac{z-A_2}{A_3}\right)^2\right]\right\}, & z<0\\ \rho_B\left\{C\exp(-z/M)\right. \\ \qquad\left.+A_1\exp\left[\left(\dfrac{z-A_2}{A_3}\right)^2\right]\right\}, & z\geq 0.\end{cases}\qquad(42)$$

One of the five parameters is eliminated by the requirement that the Gibbs dividing surface must be located at z=0. The present parametrization has four free parameters. In Table IV we show that the surface tension for the alkali metals is reduced by a half, so the comparison with the experimental values is much poorer than the results obtained with both previous parametrizations of the profile. Surprisingly the value for aluminum is very good and has changed little compared with the previous parametrizations. We can understand better the behavior of the values of the surface tension by observing the density profiles obtained with the last parametrization for sodium and aluminium. They are shown in Figs. 1(c) and 2(c), respectively. The height of the first peak of the ionic density for sodium increases substantially, rising to 1.7 times its bulk value. On the other hand, for aluminum the height of this peak is very small, and the shape of the ionic profile is similar to an exponential one.

We have tried to analyze the origin of this increase in the height of the first peak. In the first place we thought it was due to our neglect of the repulsive interaction between core electrons in pseudopotential theory. We have included the repulsive interaction via a Born-Mayer core-core potential,[30] and we found the results to be qualitatively unchanged.

Another reason for the increase in the height of the first peak could be the approximation (32) to the nonhomogeneous hard-sphere distribution function. In order to study the sensitivity of our model to this approximation we have tried other approximations for $g_{\text{hs}}(\mathbf{R},\mathbf{R}')$:

$$g_{\text{hs}}(\mathbf{R},\mathbf{R}')=g_{\text{hs}}\left(|\mathbf{R}-\mathbf{R}'|;\frac{\rho(\mathbf{R})+\rho(\mathbf{R}')}{2}\right)\qquad(43)$$

or, following Evans,[3]

$$g_{\text{hs}}(\mathbf{R},\mathbf{R}')=\tfrac{1}{2}\{g_{\text{hs}}[|\mathbf{R}-\mathbf{R}'|;\rho(\mathbf{R})]+g_{\text{hs}}[|\mathbf{R}-\mathbf{R}'|;\rho(\mathbf{R}')]\}.\qquad(44)$$

The results obtained with both improvements do not significantly change the calculated surface tensions and ionic profiles.

V. CONCLUSIONS

We have presented a theory for the surface tension of simple metals based on a perturbation expansion up to second order in the electron-ion pseudopotential. We have modified the CFN theory[9] in order to obtain a model that better describes the ionic and electronic profile oscillations. The hard-sphere fluid has been used as a reference system for the ions, and it has been shown that with this reference system and an exponential parametrized profile values for $(\partial\sigma/\partial T)_P$ close to experiment have been obtained.

The surface tension, in approximation B, is in good agreement with the experimental values if we constrain the minimization procedure to exponential or Eq. (41) parametrizations of the ionic profile. If we improve the minimization of the free energy, choosing a more flexible parametrization for the ionic profile [Eq. (42)], we find acceptable surface-tension values for polyvalent metals, but for alkali metals the results are worse, since the surface tension is halved. When we consider the ionic profile obtain with this parametrization, we can see that this drop in the surface tension is due to a large increase in the height of the first peak of the ionic density. That means that it is necessary to improve our free-energy functional.

At this moment we think that it is necessary to improve the description of the surface screening and to try to approximate the inhomogeneous electronic response function, instead of ϕ_{ind}. When approximating ϕ_{ind} we have chosen the electronic response function of a homogeneous system, with a density ρ_{ind}. This means we consider each ion surrounded with a homogeneous electron gas of density ρ_{ind}. This approximation increases the real screening between ions and makes the effective pair interaction less repulsive; so the height of the first peak is increased. In order to correct this problem it is necessary to make an approximation to the function $\phi(\mathbf{r},\mathbf{r}')$, which includes information coming from the region outside of the surface, where there are no electrons. This shortage of electrons will decrease the screening between ions and will make the interaction more repulsive, smoothing the first surface peak.

Up to now, it was believed that very accurate values of the response function of the inhomogeneous electron gas were required for the calculation of the surface tension of polyvalent metals (Foiles and Ashcroft[12]), whereas it was much less important for the alkali metals. The main conclusion of the present work is that the stability of the liquid-vapor surface for monovalent metals could be very sensitive to the values of $\phi(\mathbf{r},\mathbf{r}')$. In contrast, the polyvalent metals seem, in this respect, to be less affected by the approximations done on that function.

We are working in the implementation of an approximate inhomogeneous electron-response function similar to that used by Dobson and Rose[31] for the calculation of solid-surface properties. We hope this will prevent the exaggerated growth of the first peak for monovalent metals. We are also developing a conjugated gradient method similar to the one used in the electron reference system for minimizing the surface tension, without using any parametrized ionic profile.

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