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Perturbation theory of liquid-metal surfaces: The importance of the self-energy

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A model for the surface tension and density profile of simple liquid metals is presented. It is based on second-order perturbation theory in the electron-ion pseudopotential about the *inhomogeneous* electron gas at a jellium surface. The pair correlations in the ion fluid are computed using hard-sphere perturbation theory. The model yields good agreement with the experimental surface tensions of the alkali metals. For the polyvalent metals it is shown that it is essential to include the position-dependent self-energy of the ions, a quantity that is fortuitously small in the monovalent systems. To obtain such self-energies, very accurate values of the response function of the inhomogeneous electron gas are required.

I. INTRODUCTION

The purpose of this paper is to present a theory of the free surface of a simple (i.e., nontransition) liquid metal. This system, which contains electrons in the degenerate quantum regime and ions in the classical regime, can be reduced for most structural purposes to a classical problem similar to the inhomogeneous insulating liquid. The reduction is achieved by eliminating the electron coordinates via the Born-Oppenheimer separation. The resulting simplified problem is addressed here by generalizing the perturbation treatments developed for insulating liquids and by constructing an ionic-density functional for the liquid-metal system. The free-energy functional that emerges then permits the calculation of both the surface tension and one-body density profile.

Early work on metal surfaces has largely concentrated on the electronic aspects of the problem. These methods, often based on jellium models, replace the discrete ions by a uniform positive charge distribution which itself contains a surface. The physical attributes of the corresponding electron gas, which has the same bulk charge density as the jellium, are then computed and the surface properties of the system determined. Lang and Kohn,[1] who pioneered this approach, were primarily interested in the solid-surface problem for which a step-function profile for the jellium was appropriate. To calculate the electronic properties, they invoked a local-density approximation to the exchange and correlation contributions to the electronic energy. This method leads to a description of the electron density in terms of single-particle wave-function-like quantities that obey a Schrödinger equation incorporating an *effective* one-electron potential. They were thus able to determine the density profile and surface energy of the jellium problem. The effects of the ions (assumed later to occupy the sites of a solid lattice) are subsequently introduced by utilizing first-order perturbation theory. The resulting surface energies found by this method are in reasonable accord with experimental values.

The electron-density profile at a jellium surface exhibits Friedel oscillations that decay into the bulk. Allen and Rice[2] considered the possibility that these oscillations could actually induce similar oscillations in the *ionic*-density profile of a liquid metal. They studied this possibility by modeling the jellium as an elastic medium with its compressibility set to yield the correct bulk behavior. Calculations in the spirit of the Lang and Kohn method are then performed for different jellium-density profiles, and the total surface energy, including the elastic energy of the jellium, are subsequently computed for each profile. The surface energy is eventually minimized with respect to the ionic density to obtain the optimum surface profile. For large r_s (low density), Rice and Allen find that the ion density *does* indeed follow the electron oscillations somewhat but that the ionic profile is actually monotonic at higher densities. Further, the smooth variation of the ionic density greatly decreases the numerical contribution of electrostatic energy to the surface energy compared with that obtained for the step profile.

Other workers have approached this general problem by concentrating first on the ions. The properties of the *bulk* liquid metal can be described in terms of ions that interact with screened short-range forces, each possessing a density-dependent self-energy.[3] The electrons only enter the problem through the determination of the interactions and self-energies. Evans and Kumaravadivel[4] assumed that such a picture can even be extended into the surface region. This led them to a model ionic Hamiltonian

$$H=\sum_i \frac{p_i^2}{2M}+\sum_i u(\rho(\vec{r}_i))+\tfrac{1}{2}\sum_{i<j}[\phi(R_{ij};\rho(\vec{r}_i))+\phi(R_{ij};\rho(\vec{r}_j))]\ , \qquad (1)$$

where $u(\rho)$ is the *structure-dependent* energy per ion of a bulk metal with ionic density ρ and $\phi(r,\rho)$ is the pair potential for a bulk metal of density ρ. (Models of this type are frequently referred to as *pseudoatom models* since they attempt to map the system onto an effective neutral atomic problem.) The energetics of this model are then calculated by assuming a simple form of the two-body density, namely $\rho^{(2)}(\vec{r},\vec{r}\,')=\rho(\vec{r})\rho(\vec{r}\,')g(|\vec{r}-\vec{r}\,'|)$, with $g(r)$ given by either its bulk value or by hard-sphere values for a local density. With this ansatz, it is possible to calculate the surface tension of various liquid metals and actually to obtain reasonable agreement with experiment. However, the ansatz, which is essential, does not lead to information about the electronic degrees of freedom; it also appears to completely ignore electrostatic contributions.

Mon and Stroud[5] have also proposed a simple model for the free energy that shares the feature that it avoids explicit reference to the electronic degrees of freedom. They start with a square gradient approximation for the free-energy density functional,

$$F[\rho]=\int f(\rho(\vec{r}))d\vec{r}+\int K\,|\vec{\nabla}\rho|^2 d\vec{r}\,, \tag{2}$$

where $f(\rho)$ is the total free-energy density, *including electronic contributions,* of a bulk liquid metal of density ρ, and K is related to the direct correlation function of the liquid. In practice, a simple polynomial form for $f(\rho)$ is used which is designed to yield the correct bulk compressibility. This theory yields surface tensions in reasonably good agreement with experimental values (i.e., to within 10—20%) for both the mono- and polyvalent simple metals. Again, this treatment does not yield any information about the electron density, and again it appears to neglect certain electrostatic contributions to the surface tension.

A recent paper by Wood and Stroud[6] provides some justification for the simple model used by Mon and Stroud.[5] Starting with a uniform liquid metal they are able to show that for small variations about the uniform density, the change in the free energy of the system, correct to second order, is

$$F[\rho_i]=\int f(\rho_i(\vec{r}))d\vec{r}+\frac{k_BT}{4}\int d\vec{r}\,d\vec{r}\,'c(\,|\vec{r}-\vec{r}\,'|\,;\rho)\times[\rho(\vec{r})-\rho(\vec{r}\,')]^2\,. \tag{3}$$

This is *exactly* the same as the expression derived by Ebner, Saam, and Stroud[7] for insulating liquids, the electrons now entering directly only through $f(\rho_i)$ but indirectly through the direct correlation function of the liquid metal, $c(r)$. To obtain this result, the behavior of the electrons is described by linear response in changes from the uniform system. Wood and Stroud then further *assume* that this form will be correct even for a surface in spite of the inherent large variation in the density for this physical situation. The surface tensions that result from this assumption are in good agreement with experiment for the alkali metals, but are in somewhat poorer agreement for the polyvalent metals. These difficulties are attributed to inadequacies in the treatment of the correlation functions of the bulk liquid metals. Some of these difficulties reappear in the present work: We shall return to this important matter below.

There has been substantial effort lately to develop theories that actually incorporate both the electrons and ions explicitly, i.e., on an equivalent footing. Such approaches provide, in principle, a means of studying the dipole layer of the surface in addition to the surface tension. Evans and Hasegawa[8,9] and Amokrane *et al.*[10] have presented simple models which first start with an electron gas at a smooth jellium surface but subsequently add the effects of the ions by first-order perturbation theory. (Evans and Hasegawa[8] were even able to derive a simple analytic expression for the surface tension of their model.) Unfortunately, despite the physical appeal of these models, the resulting surface tensions are not in good agreement with experiment. The authors conjecture that the poor results reflect the need to incorporate second-order terms, i.e., screening, into the perturbation expansion. Hasegawa and Watabe[11–14] have recently carried out a set of calculations that do just that: terms to second order in perturbation theory are included and in a manner which is very similar in spirit to the work described below. They obtain good results for the surface tensions but their calculations predict that the ionic width of the surface is arbitrarily small, a feature that is clearly unphysical.

Finally, D'Evelyn and Rice[15] have performed computer-simulation studies of a pseudoatom model of liquid Na, Cs, and Hg. Again, this approach uses second-order perturbation theory to motivate a model of the energetics of the ions in a smooth electronic background. However, the authors also attempt to incorporate the fact that ions far enough from the bulk will become neutral atoms and so should not be treated by perturbation theory about an electron gas. For ions in a low-enough electronic density, however, they assume that the interactions are actually given by those of "vapor atoms." With this model, they perform Monte Carlo studies of a sphere of 256 atoms. The resulting density profiles show extremely large density oscillations, with amplitudes up to about 40% of the bulk density. It is not clear whether the large oscillations result from their basic model, the finite size of the sphere of liquid, or from insufficient convergence of the simulation. The latter possibility is suggested by similar oscillations found in simulations of insulating liquids that have been found to diminish considerably when longer simulations are performed.[16]

The method to be presented in this paper is a generalization of the perturbation treatment of the surface properties that was introduced by Abraham.[17] Section II outlines the determination of the effective Hamiltonian for the ions from the full Hamiltonian of the system. It is followed by an approximate treatment of this Hamiltonian by a combination of hard-sphere perturbation theory for the ions and density-functional theory for the electrons. Section III presents the numerical procedures and results, and the paper closes with a physical analysis of the problems associated with the calculations for the polyvalent metals, these appearing to be common in treatments of the kind given here and elsewhere.

II. DERIVATION OF THE EFFECTIVE HAMILTONIAN

Liquid metals are two-component systems consisting of electrons and ions in generally neutral ensembles. For the simple metals, the interaction between these components can be described by weak pseudopotentials which for many purposes may be taken as local. The goal of this section is to map the two-component system onto an effective ionic problem which can subsequently be treated by classical statistical mechanics. The first step in this reduction is the introduction of the adiabatic or Born-

Oppenheimer approximation according to which the Hamiltonian can be separated into two parts, namely

$$H=H_i+H_e\ , \tag{4}$$

where H_i refers solely to the ions and H_e describes the electrons *and* the electron-ion interaction. The statistical mechanics of the liquid metal are determined completely by the partition function,

$$Z=\mathrm{Tr}e^{-\beta H}\ . \tag{5}$$

The physical content of the adiabatic approximation is essentially that; because of the smallness of the electron-ion mass ratio the electrons can be well approximated as being essentially in equilibrium with the ions. This enters formally in a decomposition of the trace in the partition function, namely the trace over the electron coordinates is to be performed separately for each ionic configuration. It then follows that

$$Z\simeq\mathrm{Tr}_i e^{-\beta H_i}(\mathrm{Tr}_e e^{-\beta H_e})=\mathrm{Tr}_i e^{-\beta H_i+\beta F_e\{\vec{R}_i\}}\ , \tag{6}$$

where

$$-\beta F_e\{R_i\}=\ln\mathrm{Tr}_e e^{-\beta H_e}\ . \tag{7}$$

Here F_e is just the free energy of the electrons in the presence of the *static* collection of ions at the positions $\{\vec{R}_i\}$.

The next step is the evaluation of F_e, by perturbation theory, in orders of the electron-ion interaction. Consider the parametrized Hamiltonian

$$H=H_i+H_e(\lambda)\ , \tag{8a}$$

where

$$H_i=\sum_l\frac{P_l^2}{2m}+\frac{Z^2}{2}\sum_{l\neq l'}\frac{1}{|\vec{R}_l-\vec{R}_{l'}|}-\frac{Z^2}{2}\int\frac{\rho_i^0(\vec{r})\rho_i^0(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,d\vec{r}\,' \tag{8b}$$

and

$$\begin{aligned}H_e(\lambda)=&\sum\tfrac{1}{2}P_e^2+\tfrac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i-\vec{r}_j|}\\&+\frac{Z^2}{2}\int\frac{\rho_i^0(\vec{r})\rho_i^0(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,d\vec{r}\,'\\&+\sum_i\left[(1-\lambda)\int\frac{-Z\rho_i^0(\vec{r})}{|\vec{r}-\vec{r}_i|}d\vec{r}\right.\\&\left.+\lambda\sum_l V^{\mathrm{ps}}(\vec{r}_i-\vec{R}_l)\right]\ .\end{aligned} \tag{8c}$$

(Atomic units with energy in hartrees are used both here and in the remainder of the paper.) In (8) the l summations are over ionic coordinates, the i and j summations are over valence-electron coordinates, Z is the ionic charge, and $\rho_i^0(r)$ is an *assumed* inhomogeneous form for the ionic-number density. Now, note that for $\lambda=0$, $H_e(\lambda)$ describes a system of electrons in the presence of an *inhomogeneous* jellium background described by $\rho_i^0(\vec{r})$. This system is assumed to be well understood and is thus taken as the reference system. (In practice, the jellium problem will be addressed by the density-functional techniques used by Lang and Kohn.^{1}) For $\lambda=1$, $H_e(\lambda)$ describes the fully interacting system of electrons in the presence of a static collection of ions at $\{\vec{R}_l\}$. The free energy for $\lambda=1$ relative to the energy of the jellium system can be obtained by a coupling constant integration,

$$F_e\{\vec{R}_i\}=F_e^{\mathrm{jell}}[\rho_i^0]+\int_0^1\left\langle\frac{dH_e(\lambda)}{d\lambda}\right\rangle d\lambda\ . \tag{9}$$

To evaluate the required average, we note that the change in the potential undergone by the electrons at a given value of λ is $\lambda\Delta(\vec{r})$ where

$$\Delta(\vec{r})=\sum_l V^{\mathrm{ps}}(\vec{r}-\vec{R}_l)-\int\frac{-Z\rho_i^0(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'\ . \tag{10}$$

The average electron density is then assumed to be related to the initial electron density $\rho_e^0(r)$ by a response linear in this potential change, i.e.,

$$\begin{aligned}\rho_e(\vec{r})&\equiv\left\langle\sum_i\delta(\vec{r}-\vec{r}_i)\right\rangle_\lambda\\&\simeq\rho_e^0(\vec{r})+\lambda\int\chi(\vec{r},\vec{r}\,')\Delta(\vec{r}\,')d\vec{r}\,'\ .\end{aligned} \tag{11}$$

Here $\chi(\vec{r},\vec{r}\,')$ is the density-density response function of the *inhomogeneous* electron gas at the jellium surface. The free energy is then given by

$$\begin{aligned}F_e\{\vec{R}_i\}=&F_e^{\mathrm{jell}}[\rho_i^0]+\int\rho_e^0(\vec{r})\Delta(\vec{r})d\vec{r}\\&+\int\Delta(\vec{r})\chi(\vec{r},\vec{r}\,')\Delta(\vec{r}\,')d\vec{r}\,d\vec{r}\,'\ .\end{aligned} \tag{12}$$

We will be interested in the properties of a time-average planar surface and accordingly will consider $\rho_i^0(\vec{r})$ to vary only in the z direction [i.e., $\rho_i^0(z)$]. It is convenient to define the ionic density averaged over planes parallel to the surface:

$$\rho_i(z)=\frac{1}{A}\sum_l\delta(z-z_l)\ , \tag{13}$$

where A is the surface area. It is also useful to define the planar averaged change in the electrostatic part of the potential undergone by the electrons, i.e.,

$$\Delta_{\mathrm{es}}(z)=\int\frac{-Z[\rho_i(z')-\rho_i^0(z')]}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'\ . \tag{14}$$

The remaining change in potential is then given by

$$\Delta_r(\vec{r})=\Delta(\vec{r})-\Delta_{\mathrm{es}}(z)\ . \tag{15}$$

We now note that the free energy may be written as

$$F_e\{\vec{R}_i\}=F_e^{\rm jell}[\rho_i^0]+\int \rho_e^0(\vec{r})\Delta_{\rm es}(z)d\vec{r}+\tfrac{1}{2}\int \Delta_{\rm es}(z)\chi(\vec{r},\vec{r}\,')\Delta_{\rm es}(z')d\vec{r}\,d\vec{r}\,'$$
$$+\int \Delta_r(\vec{r})\left[\rho_e^0(\vec{r})+\int \chi(\vec{r},\vec{r}\,')\Delta_{es}(z')d\vec{r}\,'\right]d\vec{r}+\tfrac{1}{2}\int \Delta_r(\vec{r})\chi(\vec{r},\vec{r}\,')\Delta_r(\vec{r}\,')d\vec{r}\,d\vec{r}\,' \; . \qquad (16)$$

The first three terms in this expression are an expansion for the energy of a jellium surface with the jellium charge density $Z_{\rho_i}(z)$. The electron density that enters the penultimate term corresponds to a jellium density of Z_ρ as computed by linear response around the value for ρ_i^0. We now observe that the appropriate choice of ρ_i^0 is just ρ_i, the actual average ionic density. With this choice the effective Hamiltonian can be written as

$$H_{\rm eff}=H_i+F_e(\{\vec{R}_i\})$$
$$=\sum_l \frac{P_i^2}{2m}+\sum_{l\neq l'}\frac{Z^2}{|\vec{R}_l-\vec{R}_{l'}|}-\int \frac{Z^2\rho_i(z)\rho_i(z')}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,d\vec{r}\,'$$
$$+F_e^{\rm jell}[\rho_i]+\int \rho_e(z)\Delta_r(\vec{r})d\vec{r}$$
$$+\tfrac{1}{2}\int \Delta_r(\vec{r})\chi(\vec{r},\vec{r}\,')\Delta_r(\vec{r}\,')d\vec{r}\,d\vec{r}\,' \; , \qquad (17)$$

where $\rho_i(z)$ is given by Eq. (13). In practice $\rho_i(z)$ will be determined by a minimization of the surface free energy.

Note that the $\Delta_r(r)$ in this effective Hamiltonian contains summations over ionic coordinates. Thus it is clear that the penultimate term in (17) is simply a sum over one-body energies; correspondingly the last term is a sum of pair energies. It follows that this Hamiltonian has the same general form as that of an insulating liquid in the presence of an external field. The corresponding internal energy can be written in terms of the one- and two-body densities as

$$U=\tfrac{3}{2}Nk_BT+\int \rho_i(\vec{r})E^{\rm self}(\vec{r})d\vec{r}$$
$$+\tfrac{1}{2}\int \rho_i(\vec{r})\rho_i(\vec{r}\,')h(\vec{r},\vec{r}\,')\phi(\vec{r},\vec{r}\,')d\vec{r}\,d\vec{r}\,' \; , \qquad (18)$$

where

$$h(\vec{r},\vec{r}\,')=g(\vec{r},\vec{r}\,')-1 \qquad (19)$$

is the total correlation function for the ions. The self-energy in this expression is divided into two parts, i.e.,

$$E^{\rm self}(\vec{r})=\int \left[V^{\rm ps}(\vec{r}-\vec{r}\,')-\frac{(-Z)}{|\vec{r}-\vec{r}\,'|}\right]\rho_e(\vec{r}\,')d\vec{r}\,' \qquad (20a)$$
$$+\tfrac{1}{2}\int V^{\rm ps}(\vec{r}_1-\vec{r})\chi(\vec{r}_1,\vec{r}_2)$$
$$\times V^{\rm ps}(\vec{r}_2-\vec{r})d\vec{r}_1d\vec{r}_2 \; . \qquad (20b)$$

Here (20a) represents the next-to-last term in (17) and (20b) originates from the $l=l'$ contribution of the last term of (17). Note that (20b) also represents the screening self-energy of the ions. The *effective* pair interaction is thus given by

$$\phi(\vec{r},\vec{r}\,')=\frac{Z^2}{|\vec{r}-\vec{r}\,'|}+\tfrac{1}{2}\int V^{\rm ps}(\vec{r}_1-\vec{r})\chi(\vec{r}_1,\vec{r}_2)$$
$$\times V^{\rm ps}(\vec{r}_2-\vec{r}\,')d\vec{r}_1d\vec{r}_2 \; . \qquad (21)$$

We observe that the internal energy as written in (18) also has the same form as that of an insulating liquid in the presence of an external potential, except that $h=g-1$ appears here where the pair-correlation function g is normally present. This reflects the special treatment required of the overall electrostatic terms, a treatment that is required in both bulk and surface problems. The surface problem of metals also has an additional complication in that the pair interaction will depend on the position arising from the changes in the response function expected in the surface region. Section III describes the practical implementation of this physical picture.

III. THE JELLIUM ENERGY: CALCULATIONAL PROCEDURES AND APPROXIMATIONS

To evaluate the energy expression (17) for the surface problem, the surface energy and electron density are required for the jellium surface in which the background charge density is $Z_{\rho_i}(z)$. We compute these quantities by the density-functional treatment of the exchange-correlation contributions as discussed by Lang and Kohn.[1] Our calculations mostly follow theirs except for two important differences. First, the variation of the background density is not assumed to be a step function; instead it is chosen to mimic the average ionic density of the liquid surface. The second is the choice of exchange-correlation functional. Here we have used the form recently proposed by Langreth and Mehl,[18] which is designed to incorporate the dominant nonlocal corrections to the functional in a computationally convenient manner.

For practical reasons we have made one additional approximation. In the minimization of the free energy with respect to the ionic-density profile, the formalism calls for the energy of the electron gas in the presence of the *actual* charge distribution $Z_{\rho_i}(r)$. However, this density profile is obviously not known in advance; furthermore, the solution of the Lang-Kohn problem is a computationally time-consuming process. Thus, though correct in principle it is not desirable to perform such a calculation for each intermediate density profile that is encountered in the course of determining the profile that minimizes the free energy. However, in practice, this is actually not necessary. Calculations of the electron profile for ionic profiles of different widths have shown that the *electron* profiles predicted by this approach tend to be rather insensitive to the exact form of the *ionic*-density profile. It is important to note, however, that this conclusion holds only in the limit where the ionic profile is itself narrower than the electronic profile; indeed, it appears to be only substantiated firmly for the lower-density systems. On the other hand, this behavior is to be expected since the electron density cannot vary too rapidly because of kinetic energy considerations. In the limit where the ionic width is less than the minimum electron width imposed by the kinetic energy, further reductions in the ionic width cannot therefore produce similar reductions in the electron width. The electronic profile then remains largely unchanged.

As already noted this invariance does not hold in the limit of wide ionic profiles for which the electrons tend to follow the ions in order to reduce the electrostatic energy. Fortunately, we find that the liquid-metal surfaces appear to fall in the first category, and as a consequence the major shift in the energetics of the jellium problem for similar ionic profiles is just the change in electrostatic energy. Accordingly, if we have solved the jellium problem for an ionic profile $Z\rho_i^0(z)$, the surface energy of the jellium with ionic profile $Z\rho_i(z)$ is then well approximated by

$$F_e^{\text{jell}}[\rho_i] \simeq F_e^{\text{jell}}[\rho_i^0] + \Delta E_{\text{es}} , \tag{22}$$

where ΔE_{es} is the electrostatic energy change. Note that if this approximation becomes poor because of a known large difference between ρ_i and ρ_i^0, we can simply perform the Lang-Kohn calculation again using an improved estimate of the ionic density.

IV. CALCULATION OF THE IONIC ENERGY

In order to calculate the remaining contributions to the surface free energy, tractable approximations must be introduced for the ionic entropy, the pair-correlation function of the ions, and the density-density response function of the electron gas. The treatment of the first two quantities is based on the hard-sphere perturbation theory of liquids and its generalization to the insulating liquid surface by Abraham.[17] The entropy associated with a given ion should be reasonably approximated by that of a corresponding hard-sphere system with the correct local density. This leads to the simple ansatz that

$$S = \int s_{\text{HS}}(\rho_i(z))\,d\vec{r} , \tag{23}$$

where $s_{\text{HS}}(\rho_i)$ is the entropy density of a uniform hard-sphere liquid of density ρ_i. More accurate treatments of this term are possible, but since its contribution to the total surface tension is small these techniques do not at present seem necessary.

The pair-correlation function $g(r,r')$ should also be reasonably modeled by the values for a uniform hard-sphere system. Here we use a prescription based on $h(\vec{r},\vec{r}\,') = h_{\text{HS}}(|\vec{r}-\vec{r}\,'|,\rho(\vec{r}))$, a form that appears at first sight to be asymmetric in the indices $\vec{r}$ and $\vec{r}\,'$. However, it can be shown by change of variables that it is actually equivalent, in the calculation of the free energy, to the use of the average of $h(r)$ for densities $\rho(\vec{r})$ and $\rho(\vec{r}\,')$. Thus the asymmetry is only an artifact of the notation used here. This approximation for the pair correlation does, however, have a deficiency: Because of the long-wavelength capillary wave excitations of the free surface, the pair-correlation function should possess a long-range component for two points within the interface.[19] However, since the *screened* interactions in the liquid metal are actually *short ranged*, this feature should have only a small effect on the calculation of the internal energy and so is reasonably ignored here.

To approximate the electron-response function, we shall assume that the χ used to determine the energetics of a given ion is that appropriate to a uniform system but with the valence electron density taken to be that appropriate to the position of the ion. This asserts that the screening self-energy of an ion is just equal to its value for the local electron density, and further that the pair interaction is given by $\phi(\vec{r},\vec{r}\,') = \phi(|\vec{r}-\vec{r}\,'|,\rho(\vec{r}))$. In practice, it is convenient to modify this last approximation slightly and consider the product of the pair interaction and the pair-correlation function, $h(r)\phi(r)$, as a unit. This yields

$$\begin{aligned} &h(\vec{r},\vec{r}\,')\phi(\vec{r},\vec{r}\,') \\ &\qquad \simeq h_{\text{HS}}(|\vec{r}-\vec{r}\,'|;\rho_i(\vec{r}))\phi(|\vec{r}-\vec{r}\,'|,\rho_0(r)) . \end{aligned} \tag{24}$$

Again the apparent asymmetry in the indices can be removed by a change of variables.

In the numerical computations, it is convenient to regroup the terms somewhat in order to generate the free-energy density of a uniform system together with corrections. This produces the following form of the free-energy functional:

$$F = F_e^{\text{jell}}[\rho_i] + \int f(\vec{r})\,d\vec{r} , \tag{25}$$

where

$$\begin{aligned} f(\vec{r}) = f^{\text{bulk}}(\rho_i(\vec{r}),\rho_e(\vec{r})) &+ \rho_i(\vec{r}) \int \left[V^{\text{ps}}(\vec{r}\,'-\vec{r}) - \frac{Z}{|\vec{r}\,'-\vec{r}|} \right] [\rho_e(\vec{r}\,')-\rho_e(\vec{r})]\,d\vec{r}\,' \\ &+ \tfrac{1}{2}\rho_i(\vec{r}) \int [\rho_i(\vec{r}\,')-\rho_i(\vec{r})]\,h(|\vec{r}-\vec{r}\,'|,\rho_i(\vec{r}))\phi(|\vec{r}-\vec{r}\,'|,\rho_e(\vec{r}))\,d\vec{r}\,' . \end{aligned}$$

In this expression, f^{bulk} is the free-energy density, excluding electrostatic terms, of a bulk liquid metal with ionic and electronic densities, ρ_i and ρ_e.

In calculating the properties of the various uniform systems further approximations are necessary. First, the bulk response function is taken to be consistent with the local density approximation for the exchange-correlation energy. This has been shown by Rose and Dobson[20] to be

$$\chi(k)=\frac{\chi^0(k)}{1-(4\pi/k^2+G)\chi_0(k)}\ , \tag{26}$$

where

$$G=\frac{d^2}{d\rho_e^2}\rho_e\epsilon_{\mathrm{xc}}(\rho_e)\ .$$

In these expressions $\epsilon_{\mathrm{xc}}(\rho_e)$ is the exchange-correlation energy per particle of the uniform electron gas and χ_0 is the Lindhard function. Next, as a representative local pseudopotential we use the empty-core model[21]

$$V^{\mathrm{ps}}(r)=\begin{cases}0, & r<R_c\\ -Z/r, & r>R_c\ .\end{cases} \tag{27}$$

Here R_c is a core radius which we have chosen to eventually be consistent with a hard-sphere packing fraction of $\eta=0.47$. (The resulting core radii are similar to those computed by other methods.[22]) In addition, the $k=0$ value of the pseudopotential is adjusted separately to yield the correct equilibrium density. The hard-sphere correlation functions that we require are obtained from the parametrizations of Verlet and Weis,[23] and of Henderson and Grundke,[24] and the hard-sphere free-energy density is derived from the Carnahan-Starling[25] equation of state which is thermodynamically consistent with these correlation functions. Finally, the hard-sphere diameter used for a given set of densities is determined by the criteria used in the Weeks, Chandler, and Anderson[26] perturbation theory of bulk liquids.

Lastly, note that what we have obtained is an expression for the free energy of a liquid metal with a surface. However, the experimental quantity of interest is the surface tension itself, γ. The latter is normally equal to the excess surface free energy computed relative to the Gibbs dividing surface (i.e., zero excess number). For a *general* two-component liquid, however, one cannot normally define a *single* dividing surface such that the excess number of *both* components vanish. However, since we assume here that the metal surface is *charge neutral,* a single Gibbs dividing surface can indeed be defined in such a way that both the electrons and ion excess numbers vanish.

V. RESULTS FOR THE ALKALI METALS

The procedures just described have been applied to the alkali metals, Na, K, Rb, and Cs. Table I lists the bulk densities, temperatures, and pseudopotential core radii used in the calculations. The temperatures and densities correspond to the zero-pressure melting points in all cases. For reference, the bulk compressibilities and the core radii quoted by Cohen and Heine[22] for these systems are also listed.

The ionic profile is assumed to have the parametrized form

$$\rho_i(z)=\rho_0\begin{cases}1-\frac{1}{2}e^{z/w}, & z<0\\ \frac{1}{2}e^{-z/w}, & z>0\ .\end{cases} \tag{28}$$

TABLE I. The experimental electron density, temperature, and compressibility of the liquid metals at the melting point. The last column lists the pseudopotential core radius, and the value from Ref. 12 in parentheses.

	ρ_e (a_0^{-3})	T (K)	$\dfrac{K_T}{\rho k_B T}$	R_c
Na	3.60×10^{-3}	371	0.023	1.73 (1.66)
K	1.88×10^{-3}	337	0.024	2.27 (2.12)
Rb	1.54×10^{-3}	312	0.022	2.49 (2.12) (2.72)
Cs	1.23×10^{-3}	302	0.024	2.71 (2.93)
Mg	1.17×10^{-2}	923	0.025	1.39 (1.39)
Zn	1.79×10^{-2}	693	0.015	0.98 (1.27)

For this profile, the 10—90 width, which is the width that will be referred to below, is $w_{10-90}=3.2a_0$. A simple monotonic form of this kind does not allow us to investigate the possibility of oscillatory behavior in the density profile. If present, this behavior is expected to have only a small effect on the energetics of the surface.[9] On the other hand, it is not clear that the present method can definitively address the question of oscillatory behavior in the one-particle density even with the introduction of a more general form for the profile. Nevertheless, it should allow us to determine an approximate width of the interfacial region as well as the surface tension.

The surface tensions and widths computed for the liquid alkali metals are presented in Table II along with the experimental surface tensions. Also included in the table is the surface energy of the jellium component, with the minimizing ionic density and the contribution of the ionic-density functional (16) to the surface tension. Figure 1 shows both the electronic- and ionic-density profiles for Na. As expected the ionic profile is narrower than the electronic profile. The profiles for the other alkali metals are similar.

As can be seen from Table I, the surface tensions are all somewhat above the experimental values but still in good agreement with them. Part of the calculated difference may be attributable, as noted, to the free energy of capillary waves. (This perturbative treatment of the surface tension concentrates on the local energetics and so does

TABLE II. The computed 10—90 surface widths and theoretical and experimental surface tensions of the liquid alkali metals. The decomposition into σ_{jell} and σ_{ion} is defined in the text.

	w (a_0)	σ_{jell}	σ_{ion}	σ_{theor}	σ_{expt}
Na	5.8	144	66	210	191
K	5.3	92	29	121	115
Rb	5.6	75	32	107	85
Cs	5.7	64	26	90	70

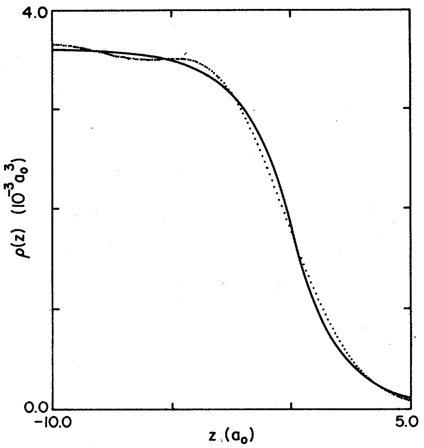

FIG. 1. Ionic (——) and electronic (· · ·) number density at the Na surface.

not appear to include the contributions from the capillary wave excitations of the surface.) In the absence of external fields, the capillary wave contribution[27] is of order

$$\Delta\gamma \simeq \frac{-(1/\omega)^2}{4\pi\beta} \ . \tag{29}$$

Using the above estimates of the width, we find that this correction is negative and with a magnitude of a few ergs/cm^2. Thus it is plausible that much of the discrepancy between theory and experiment in this case may be indeed due to the neglect of such capillary excitations.

The ionic widths predicted for the alkali metals are substantially less than those calculated from the theory of Mon and Stroud[5] but, on the other hand, are considerably wider than the step profiles predicted by Hasegawa and Watabe.[11] The only experimental data available on the widths of the alkali-metal surfaces are the recent reflectivity experiments on Cs by Sluis and Rice.[28] Unfortunately, these authors do not fit their data to a monotonic density profile. However, we can infer from their comparisons with the predictions of the Mon and Stroud theory that the width is substantially less than those predictions and thus plausibly consistent with our results. Note further that for K, Rb, and Cs, the widths increase as we expect, since the length scales of the electron gas are also increasing. Sodium, with the highest electron density, does not fit this trend. A possible explanation for this will be discussed below.

Recall that the electron density is computed for an assumed ionic profile and that the jellium energy is taken from this calculation together with the change in electrostatic energy corresponding to the ionic profile being considered. To assess the sensitivity of the method to the choice of initial profile, the Na calculation was performed again with an *assumed* ionic 10—90 width of $3.2a_0$ and $4.8a_0$. The resulting surface tensions are 214 and 210 ergs/cm^2, respectively, and thus appear not to depend appreciably on the choice of the ionic density used in the jellium calculation. For the other alkali metals, the jellium calculations were performed with an initial profile width $w_{10-90} = 6.4a_0$.

VI. THE POLYVALENT METALS

This procedure can also be applied to the divalent metals Mg and Zn, but in common with other approaches to this problem the results of the procedure just described for these systems are not satisfactory. The surface tensions are predicted to be negative and the widths to be large (for example, $w_{10-90} > 6a_0$ for Mg). The former conclusion is clearly wrong (the experimental surface tensions are 559 ergs/cm for Mg and 782 ergs/cm for Zn). The latter conclusion violates the physical intuition that smaller r_s systems should have narrower surfaces. The appearance of large widths actually prevents any reliable determination of surface values for this model since ionic widths are required that are larger than the relaxation widths of the electronic system. Thus the approximation (22) for the calculation of the jellium energy for $\rho_i(z)$ by simply correcting the electrostatic contributions for the calculation with $\rho_i^0(z)$ is clearly inadequate. It is also clear, though, that the resulting surface tensions will inevitably be strongly negative ($\gamma \lesssim -100$ ergs/cm^2). This conclusion follows from noting that the surface tensions calculated for a given initial width are large and negative to begin with. The width that later minimizes the surface energy is always greater than the assumed initial width, and the larger the assumed initial width, the more negative the surface tension is then computed to be.

Negative surface tensions are in part attributable to wide ionic profiles and are directly traceable to the electron gas surface energy. We recall that for small r_s, the jellium surface energy at a step surface is itself negative[1] and is a direct consequence of the reduction of the electronic kinetic energy at the surface. With a smooth profile, however, the kinetic energy savings can be substantial. In real systems, the background charge is not continuous but discrete (the ions) and the positive surface tensions in metals with small r_s result principally from the increase in the ionic self-energy as the ions approach the surface. The fact that the surface tension is negative in the scheme presented above therefore implies that either the reduction in kinetic energy has been overestimated or the increase in ionic self-energy has been underestimated. We shall argue below that the latter is the case.

The theory of surface properties of the polyvalent metals have thus been more of a challenge than is the case for the alkali metals. Though we now understand the reasons, to a certain extent the challenge persists. But consider the following. A fundamental difference between the polyvalent metals and the alkali metals is the relative size of the ionic-density-functional contribution to the total surface tension. The surface energy of the electrons in jellium for a step jellium profile is greatest for $r_s = 3.0$—3.5 and thereafter decreases rapidly for higher densities. It even becomes negative for $r_s < 2.5$. As mentioned above, the jellium energies are themselves lower for a smoothly varying ionic profile. As a result, the ionic-density-functional contribution to the surface tension of the polyvalents is obviously of the same order or even larger than the *total* surface tension. This is in striking contrast to the alkali metals, where the ionic contribution is only about a quarter of the total. From this it is apparent that the ionic-density functional itself should be an order of magnitude larger in the polyvalent metals than in the corresponding case in the alkali metals. Further, since the jellium energy will favor broad ionic profiles, the energy barrier required to maintain a reasonable surface width must also come from the ionic-density functional. The failure of the model for this case therefore clearly indicates that the density functional as treated above is in some way deficient. We may also note that the somewhat anomalous width computed for Na may also reflect similar problems since of all the alkali metals its electron density is highest and hence closest to the polyvalents.

One possible source of the evident difficulties in the polyvalent metals is the treatment of the pair interactions, but this does not seem likely for various reasons. First, the total contribution of the pair interactions to the surface energy can be easily estimated. Each surface atom loses about half its bonds (about six) with each bond having an energy roughly equal to the depth of the potential which, for example, is about 0.002 hartree for Mg. The pair contribution to the surface tension then is approximately this energy per atom divided by the surface area occupied by each atom. This gives a value of about 100 ergs/cm^2 for Mg. It therefore seems unlikely that small errors in the treatment of this contribution can lead to the large energies needed to correct the deficiencies. As a further test, the characteristic pseudopotential radius r_c can be changed; however, the resulting general behavior does not. Finally, the bulk response function can also be altered, for example, to the form proposed by Singwi, Sjölander, Tosi, and Land;[29] but once again the general behavior remains unchanged. Since these changes must also alter the pair interaction, this further supports the conclusion that the problem is *not* with the pair contribution.

We are therefore led to consider the one-body terms, i.e., the self-energy of the ions, which represents a *very large* contribution to the total energy. In particular, we observe that the screening contribution to the self-energy varies by about a hartree (2 Ry) as the position of the ion varies through the interface. Further, the common assertion that this term can be computed *solely* from a knowledge of the *local* electron density, though initially plausible, is actually suspect since the screening length is comparable to the width of the electronic profile. In order to assess the reliability of the local approximation for the screening energy, a simple yet reasonable approximation for the screening self-energy is desired.

The screening self-energy can be written as an integral in real space, namely

$$E_{\mathrm{sc}}^{\mathrm{self}}(\vec{\mathrm{r}})=\tfrac{1}{2}\int V(\vec{\mathrm{r}}_1-\vec{\mathrm{r}})\chi(\vec{\mathrm{r}}_1,\vec{\mathrm{r}}_2)V(\vec{\mathrm{r}}_2-\vec{\mathrm{r}})d\vec{\mathrm{r}}_1 d\vec{\mathrm{r}}_2\ . \tag{30}$$

The local approximation simply sets $\chi(\vec{\mathrm{r}}_1,\vec{\mathrm{r}}_2)=\chi(|\vec{\mathrm{r}}_1-\vec{\mathrm{r}}_2|,\rho(\vec{\mathrm{r}}))$. This form has the obvious disadvantage that the density response between two points depends on the position of the ions. That is clearly not correct. A simple model for χ that is both reasonable and computationally convenient averages the bulk response functions for the local densities at $\vec{\mathrm{r}}_1$ and $\vec{\mathrm{r}}_2$, i.e.,

$$\chi(\vec{\mathrm{r}}_1,\vec{\mathrm{r}}_2)\simeq\tfrac{1}{2}[\chi(|\vec{\mathrm{r}}_1-\vec{\mathrm{r}}_2|,\rho_e(\vec{\mathrm{r}}_1))+\chi(|\vec{\mathrm{r}}_1-\vec{\mathrm{r}}_2|,\rho_e(\vec{\mathrm{r}}_2))]\ . \tag{31}$$

When placed into the self-energy expression this leads, after a change of variables, to

$$\begin{aligned}E_{\mathrm{sc}}^{\mathrm{self}}(\vec{\mathrm{r}})=\tfrac{1}{2}\int V(\vec{\mathrm{r}}_1-\vec{\mathrm{r}})\chi(|\vec{\mathrm{r}}_1-\vec{\mathrm{r}}_2|,\rho(\vec{\mathrm{r}}_1))\\ \times V(\vec{\mathrm{r}}_2-\vec{\mathrm{r}})d\vec{\mathrm{r}}_1 d\vec{\mathrm{r}}_2\ .\end{aligned} \tag{32}$$

The simplest model of the bulk response function is the Thomas-Fermi screening result, namely,

$$\chi(k)=-\frac{k_0^2}{4\pi}\left[1-\frac{k_0^2}{k_0^2+k^2}\right], \tag{33}$$

where k_0 is the Thomas-Fermi wavelength, i.e.,

$$k_0=2(3/\pi)^{1/6}\rho_e^{1/6}\ .$$

If the electron-ion interaction is taken to be purely Coulombic, the expression (32) can be evaluated in closed form for the uniform system, i.e.,

$$E_{\mathrm{sc}}^{\mathrm{self}}=-\frac{z^2}{2}k_0\ . \tag{34}$$

For the nonuniform case, all of the integrals can be performed analytically except for the final z_1 integration. To see this, we first take the Fourier transform in the plane perpendicular to z. This yields

$$\begin{aligned}E_{\mathrm{sc}}^{\mathrm{self}}(z)=\frac{1}{8\pi^2}\int dz_1 dz_2\int d^2Q V(z_1-z,\vec{\mathrm{Q}})\\ \times\chi(z_1-z_2,\vec{\mathrm{Q}})V(z_2-z,\vec{\mathrm{Q}})\ ,\end{aligned} \tag{35}$$

where the Coulomb potential takes the form

$$V(z,Q)=2\pi Z\frac{e^{-Q|z|}}{Q} \tag{36}$$

and the response function is

$$4\pi\chi(z_1 a)=-k_0^2\delta(z)+\frac{k_0^4}{2}\frac{\exp[(Q^2+k_1^2)^{1/2}|z|]}{\sqrt{Q^2+k_0^2}}\ . \tag{37}$$

Next, the integral over z_2 is carried out (taking care to treat the absolute values correctly). After combining terms and simplifying, we obtain

$$E_{\mathrm{sc}}^{\mathrm{self}}(z)=-\frac{z^2}{4}\int_{-\infty}^{\infty}k_0^2(z_1)\int_0^{\infty}\frac{\exp\{-[Q+(Q^2+{k_0}^2)^{1/2}]|z_1-z|\}}{\sqrt{Q^2+k_0^2}}dQ\,dz_1\ . \tag{38}$$

Note that the k_0 in this expression depends on the position z_1 through its dependence on $\rho(z_1)$. The integral over Q can now be simplified by the change of variables $\eta = Q + \sqrt{Q^2 + k_1^2}$. The result can be even further simplified thereafter to give

$$E_{\text{sc}}^{\text{self}}(z) = -\frac{Z^2}{4} \int_{-\infty}^{\infty} k_0^2(z_1) \int_{k_0|z_1 - z|}^{\infty} \frac{e^{-t}}{t} dt\, dz_1 \ . \tag{39}$$

This integral is the exponential integral E_1 for which there exist accurate rational approximations.[30] We thus obtain the final expression,

$$E_{\text{sc}}^{\text{self}}(z) = -\frac{Z^2}{4} \int_{-\infty}^{\infty} k_0^2(z_1) E_1(k_0(z_1)\,|z_1 - z|\,) dz_1 \tag{40}$$

with

$$k_0(z_1) = 2[(3/\pi)\rho_e(z_1)]^{1/6} \ .$$

With this expression it is very straightforward to numerically evaluate the self-energy as a function of position given as primary input a form for the electron density. For the calculations below, a simple fit to the electron density of the Mg surface can be used, namely

$$\rho_e(z) = \rho_0[1 - \tanh(0.8z)] \ . \tag{41}$$

The resulting self-energy for both the nonlocal approximation (40) and local approximation using (34) are plotted in Fig. 2. The difference between these two values is presented in Fig. 3.

These results lead to two qualitative but extremely important conclusions. First, the nonlocal self-energy rises much more rapidly in the vicinity of the surface than is the case for the local approximation. This strongly favors a *narrower* surface and so tends to explain the wide profiles obtained above. Second, the nonlocal self-energy is substantially *below* the local value and hence more energetically favorable for ions close to the surface. This will, of course, lower the surface tension even further. However, it is now possible to isolate the physical reasons behind the difficulties encountered in the polyvalent metals.

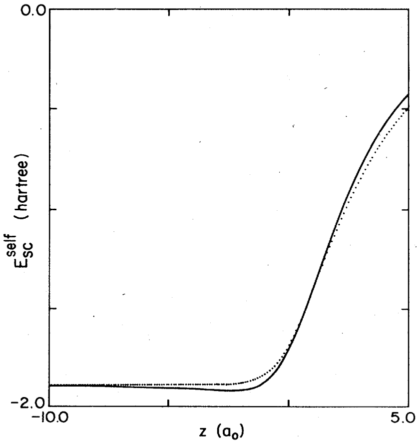

FIG. 2. Position-dependent ionic screening self-energy for Mg. Solid curve is nonlocal approximation (258) and dotted curve is local approximation.

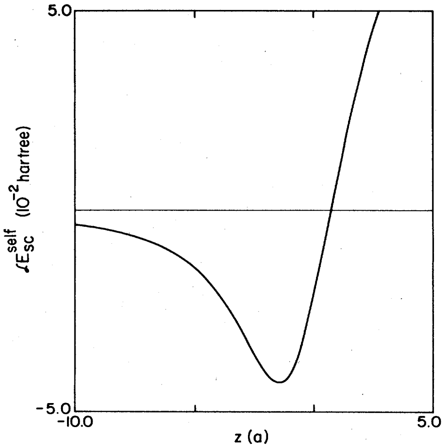

FIG. 3. Difference between the nonlocal and local approximations to the ionic self-energy.

To assess the reliability of these calculations, two changes can easily be considered. First, the pure Coulomb potential can be replaced by a pseudopotential. The empty-core potential is analytically inconvenient for this calculation; the form

$$V^{\text{ps}}(r) = -\frac{Z}{r}(1 - e^{-\lambda r}) \tag{42}$$

is more convenient and has the correct qualitative behavior for the purposes of this argument. A similar nonlocal analysis of the self-energy can then be performed except that the Q integral must now be evaluated numerically. The difference between the resulting nonlocal and local approximations is almost the same as that computed for the pure Coulomb potential. (The self-energy values themselves are quite different, though.) This reflects the fact that the pseudopotential only differs from the Coulomb potential at short distances where the local approximation is reasonable. Thus the effects of the pseudopotential largely cancel in the difference.

The sensitivity of these results to the form of the *bulk response functions* can also be determined (the Thomas-Fermi response function is rather crude, especially for large k). Recently, Igloi[31] has proposed a simple analytic form for $\chi(k)$ that correctly describes both the large and small k limits, namely

$$\chi(k) = \frac{-P(k)}{1 + (4\pi/k^2)P(k)} \ , \tag{43}$$

where

$$P(k) = \frac{k_F}{\pi^2} \frac{\delta}{[1 + 3\delta(k/2k_F)]^2} \tag{44}$$

and

$$\delta = \left[1 - \frac{1 + 0.0155/k_F}{\pi k_F}\right]^{-1} \ . \tag{45}$$

A calculation, with the Coulomb potential, similar to the one described above which can also be performed for this response function though the Q integral, must again be carried out numerically. The resulting difference in the local and nonlocal self-energies is again very similar to Fig. 3. This suggests that the exact form of the bulk response function used in this approach also does not affect the difference between the local and nonlocal treatments. [Note that (44) contains a parameter δ which is ill-defined in the low-density limit. Nevertheless, in this limit the self-energies are quite insensitive to the choice of δ.]

A large decrease in the nonlocal estimate of the self-energy for ions near the surface is somewhat counterintuitive. In addition, if valid it would imply vastly negative surface tensions. The above analysis clearly suggests that this conclusion follows from the ansatz (31) relating the inhomogeneous response function to the bulk values. As the bulk density changes, the response function varies in two ways. First, the amplitude of χ varies as the cube root of the density. This reflects the requirement that if there is less material present, the response to a potential change will be smaller. The second change in χ is the variation of its basic length scale. It is clear that the change in amplitude can only lead to an *increase* in the self-energy so any anomalous decrease must itself be attributable to the change in the length scale. It is not clear that it is physically correct to incorporate this change of length scale into the response for electrons at the edge of the metal. In particular, the divergence of the length scale that occurs for zero electron density is physically inappropriate. Also, since the electrons in the tail of the profile cannot really be distinguished from those in the bulk, the basic length scale may in fact be much more representative of that of the bulk. These arguments then suggest that the variation of the length scale of the response function is too strong. To see if a slower and bounded variation of the length scale will lead to more reasonable behavior, the following alternative can be studied:

$$E^{\mathrm{self}}_{\mathrm{sc}}(z) = -\frac{Z^2}{4}\int_{-\infty} k_0^2(z_1)E_1\{[\alpha k_0^{\mathrm{bulk}} + (1-\alpha)k_0(z_1)]\,|z_1 - z|\,\}dz_1 \ ,$$

where α is a weight that roughly determines how much the length scale should vary. A straightforward calculation then shows that the self-energies determined from this form do *not* in fact have the anomalous decrease in the self-energy near the surface. However, they still retain the more rapid increase of the self-energy near the surface *compared with the local approximation,* a clear indication that this feature is probably correct since it is not affected by the various modifications to the model. To establish if such a change in the self-energy would actually correct the predictions of the surface model for Mg, the difference in the local and nonlocal self-energies can simply be added to the self-energies used in the original surface calculations. For $\alpha = 0.15$, the surface tension thus computed for Mg agrees with experiment; the 10—90 width is then $4.5a_0$. This width seems physically plausible in that it is somewhat less than the widths inferred for the alkali metals as one expects because of the shorter response length of the electron gas. Experimental information on the widths could be extremely useful to check this expectation.

Note that in principle any substantial changes in the calculated values of the self-energy can destroy the already reasonable results we have obtained for the alkali metals. However, the central point is that the ionic self-energies make a much *smaller* contribution to the surface tension in these metals because the self-energy for a given electron-ion potential decreases with the electron density. This, coupled with the factor of Z^2 scaling the interactions, implies that the self-energies are about an order of magnitude smaller for the alkali metals. Further, the contribution of a given change in the self-energy on the surface tension is also proportional to the ionic density. This is again substantially lower for the alkali metals. Accordingly, we do not expect that changes in the calculation of the ionic self-energies will make a significant difference in the results for the alkali metals.

The nonlocal model for the self-energy just described is not intended as an accurate theory of that quantity. It does strongly suggest, however, that the local approximation radically underestimates the rise of the self-energy as the ionic position is moved through the surface and that this underestimation is principally responsible for the negative surface tensions obtained for the polyvalent metals using the procedure described earlier. Further, the results from the nonlocal model strongly suggest that a more realistic treatment of the self-energy may lead to results for the polyvalent metals that in turn lead to agreement with experiment. The next step toward understanding these systems is thus an accurate calculation of the screening self-energy as a function of position in the interface. This requires an accurate knowledge of the response function of an electron gas at a jellium surface. Only when these results become available will it be possible to make a determination of the surface properties of the polyvalent metals of an accuracy comparable to that currently achievable for the alkali metals.

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