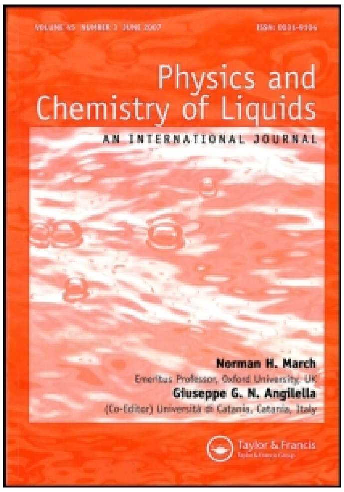

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# Surface Tension Calculations for Liquid Metals

J. -P. Badiali[a]; A. Lepape[a]; J. Goodisman[b]
[a] Physique des Liquides et Electrochemie, Université Pierre et Marie Curie, Paris, Cedex, France [b] Department of Chemistry, Syracuse University, New York, U.S.A.

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# Surface Tension Calculations for Liquid Metals

J.-P. BADIALI and A. LEPAPE
*Physique des Liquides et Electrochemie, Université Pierre et Marie Curie, 4, Place Jussieu 75230 Paris, Cedex 05 France.*

and

J. GOODISMAN
*Department of Chemistry, Syracuse University, New York 13210 U.S.A.*

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We present a class of models for the surface of a liquid metal, which may be part of an electrochemical interface. The particles of the system, for the purpose of derivation of thermodynamic properties, are the charged ion cores, while the energy of the electrons is evaluated using the electron density functional formalism, previously principally applied to solids. An expression for the surface energy $U^s$, defined as the energy required to create unit area of surface by separation of a volume of homogeneous metal into two parts, is derived (Eqs. 18–20). The surface tension $\gamma$ is obtained by differentiating the Helmholtz free energy with respect to the area of the system, keeping volume and particle number constant (Eqs. 27–37). The surface tension is also equal to the difference between the free energy of the system containing a surface and the free energy of a reference system. It thus defines a surface energy through the Gibbs–Helmholtz equation, and this surface energy is shown to be identical to $U^s$.

The expressions for $U^s$ and $\gamma$ are made explicit (Eqs. 45–57) by insertion of particular assumptions for the ion-density profile, the electron-density profile, the interionic interaction and pair distribution function, and the electronic energy. Only information about bulk liquid metal is used. The parameter in the electron-density profile is obtained by minimizing the surface energy. The simplest assumption for the interionic interaction, hard-sphere and Coulombic repulsions, requires a choice for the hard-sphere diameter, which is made such that the pressure of bulk metals is given correctly (52–55). For the alkali metals, the surface tension calculated from this model is about half the experimental value in each case, while calculated surface energies are too high ($\frac{1}{5}$ too high for Cs, but three times too high for Li). For the electrical potential difference between the inside and the outside of a metal, and for the electrochemical potential, agreement with experiment is good. The main reason for the disagreements in the other properties is traced to the simple form used for the ion pair distribution function.

## INTRODUCTION

The electrochemical interface consists of a metal in contact with an electrolyte. In the case of a polarisable electrode, changes in properties of the interface due to changes in the potential difference across it are interpreted to give information about the distribution of components of the electrolyte.[1] The metal, usually Hg, is taken as a structureless charged surface. To investigate whether the metal's structure indeed makes no contribution, a model for the surface of liquid metal is needed, which can give surface tension, as well as electrical properties, for different states of charge.

A statistical mechanical calculation of surface tension requires, first of all, the interaction potentials, which one can derive from the properties of the homogeneous phases. The interionic potential for a liquid metal represents an effective interaction, which includes the effects of the electron gas. In the presence of a surface, the electronic wave functions differ markedly from plane waves, and the effective interionic potential appropriate to the homogeneous phase cannot be used. We will assume only that the bare electron-ion pesudo-potential remains valid in the interface.[2–4] Clearly, it is a more complex problem to calculate the surface tension for a simple metal than for a non-metal.

Two approaches suggest themselves. The first is based on the electron density functional formalism,[5] and has principally been applied to solids. Lang and Kohn[2] use this theory to calculate electron density profiles for alkali metals with the ions being represented by a jellium model. The calculated surface energies compare well to the surface tensions of the liquids extrapolated to 0°K but become negative for dense metals. The problem can be corrected by treating the interaction between ions and electrons in detail. Lang and Kohn assume that the difference between the interaction energy for a lattice of ions and the corresponding quantity for the jellium model, can be calculated by first-order perturbation theory. The known lattice structure of the solid is used in carrying out this calculation, and the electron density profile associated with the jellium is maintained.

For the calculation of work functions J. R. Smith[6] employs a similar scheme. However, the electron density profile is never calculated, but given an assumed form, with parameters chosen to optimize the surface energy calculated for the jellium model. Reasonable results are obtained. Using Smith's method. G. Paasch and collaborators[7] calculated work functions, determining the electron density profile by taking into account a lattice of ions, including a relaxation of the position of the last lattice plane. This gives profiles which differ noticeably from Smith's. Allen and Rice [7a] have used the Lang–Kohn formalism to discuss the ion-density profile for a liquid metal surface.

A second approach, specific to the liquid state, has been proposed by

R. Evans.[4,8] It involves the extension to a surface region of a pseudo-ion model which is valid for homogeneous systems. The electron density profile is here taken as fixed; it must be determined by the Smith or Lang–Kohn models, i.e., independently of the Evans theory. Evans' theory gives measurable properties of the correct size. However, the fact that the electronic profile is not determined in a self-consistent manner, and the difficulty of defining a surface potential, represent two disadvantages from the point of view of our intended application. The surface potential is a natural quantity in a density functional treatment, but calculation of surface tension presents new problems.

We propose a class of models which, on one hand, employ a density functional formalism for the conduction electrons, and, on the other hand, specifically take into account the structure of the liquid state through the interionic correlation function. In Section I, we derive such models from the partition function for a system of electrons and ions. This permits us to make explicit our general assumptions. The electron density functional is introduced in Section II. In Section III, we derive formulas for surface tension and surface energy, taking into account the effect of changing surface area on the electron density profile. The relation between surface tension and surface energy, and the determination of parameters in a simple model, are discussed in Section IV. In Section V we present some results for the alkali metals in the absence of external field. Some discussion follows in Section VI. In an Appendix, the effect of using a more complex density profile is shown.

## I DERIVATION OF THE MODEL

Let us consider a system of heavy charged particles and electrons, the number of each being fixed. The properties of the system at fixed temperature and volume can be derived from the canonical partition function which involves a sum over states for the electrons, described by quantum mechanics, and integrations over momenta and configuration space ($\Gamma$) for the heavy particles, described by classical mechanics, and referred to here as ions (see below).

$$Q = \frac{1}{N!}\int \mathrm{d}P_N\,\mathrm{d}\Gamma \sum_i g_i \exp\left\{-\beta\left[E_i(\Gamma) + F_2(\Gamma) + \frac{\Sigma P_k^2}{2M}\right]\right\} \tag{1}$$

According to the Born–Oppenheimer separation of electronic and nuclear motions,[9] the electronic Schrödinger equation is considered to be solved for each ionic configuration $\Gamma$, giving a series of eigenenergies $E_i$ with degeneracies or multiplicities $g_i$. The Hamiltonian in the Schrödinger equation includes the potential due to the ions, so that $E_i$ includes the ion-electron interaction. The ion-ion interactions, represented by $F_2$, must be added to this $E_i$, and so must the ionic kinetic energy, $P_k^2/2M$ for each ion $k$, with $M$ being the ionic mass. Of course, $\beta = 1/kT$. The integrations over ionic momenta are trivial in (1), yielding a factor of $(2\pi M/h^2\beta)^{3/2}$ for each ion.

Next, we assume that, for every ionic configuration $\Gamma$ of importance, the difference between the lowest and next lowest electronic energies is large compared to $kT$, so that the sum of (1) is reduced to the term for $i = 0$. The ground state being non-degenerate,

$$Q = \frac{1}{N!}\left(\frac{2\pi M}{h^2\beta}\right)^{3N/2} \int \mathrm{d}\Gamma e^{-\beta[E_0(\Gamma)+F_2(\Gamma)]} \tag{2}$$

According to the theorem of Kohn and Hohenberg,[10] the ground state energy for each $\Gamma$ is a functional of the electron density $n$; if the functional were known, one could determine the electron density and $E_0$ by a variational procedure. The energy $E_0$ depends on the ionic configuration directly through the ion-electron term in the Hamiltonian, and indirectly, since it is the eigenvalue of a Hamiltonian (for the electronic Schrödinger equation) which depends on the ionic configuration. Similarly for the density-functional formalism, we separate out direct and indirect (through $n$) dependences of $E_0$ on $\Gamma$, writing

$$E_0 = E_0[n(\Gamma), \Gamma] = \sum_i F_1(n(\Gamma), \mathbf{R}_i) + R_0[n(\Gamma)] \tag{3}$$

Here $\mathbf{R}_i$ gives the position of ion $i$. Because of the equivalence of the ions, $n$ actually depends on the ionic distribution $\rho^{(1)}$ rather than the configuration. If $\rho^{(1)}$ displays planar symmetry, so will $n$.

The heavy particles which we refer to as ions will actually represent the ionic cores of the liquid metal, and the electrons will be the conduction electrons only. Since the ionic cores themselves involve electrons, the electronic energy cannot really be treated as we have done. We will assume, however, that one may invoke a first-order pseudopotential theory and write $E_0$ as in Eq. (3), with $F_0(n(\Gamma))$ representing the properties of the gas of conduction electrons alone and $F_1(n(\Gamma), \mathbf{R}_i)$ representing the interaction (via a pseudopotential) of the electron gas with the ion core located at $\mathbf{R}_i$. Below we will use, as did Lang and Kohn[2] and Evans,[4] an Ashcroft-type pseudopotential.[11] Mathematical manipulations are easy with this potential, which involves only the core radius $R_c$, and describes at least qualitatively certain important physical properties.[11] Our model could, of course, be used with pseudopotentials of other forms. Cohen and Heine[12] have shown how pseudopotentials can be parameterized on the basis of experimental results. Their numerous tabulations demonstrate the range of variation of the parameters.

If we limited ourselves strictly to a first-order theory, $F_2[\Gamma]$ would be simply the direct interionic interaction, composed of a short-range core repulsion and a Coulombic repulsion. The core radius required to represent the former by a hard-sphere interaction would be d $\approx 2R_c$. For the homogeneous phase, the first-order pseudopotential theory gives good approximate results for certain thermodynamic properties.[13] It is quite incapable of correctly describing structural properties. Rather, it is the second-order terms, modifying the effective interionic potential, which determine the atomic arrangements.

Various authors[14] have discussed the derivation of an effective local pair potential for the ions starting from the self-consistent energy (a sum of one-electron energies for the conduction electrons, the bare-ion electrostatic repulsion, and a correction for double counting of interelectronic repulsion). The effects of the ion-electron pseudopotential (bare-ion potential plus screening), included to second order, lead to an oscillatory ionic pair potential. Waseda and Suzuki,[15] starting with structural data for the liquid alkali metals, derived interionic pair potentials by solving the Born–Green–Yvon equation. The potentials include long-range oscillatory parts, but it was noted that, at temperatures just above the melting point, the hard-sphere potentials as parameterized by Ashcroft and Lekner[16] led to structure factors nearly the same as those from the more complicated potentials.

In the presence of a surface, it is evident that the second-order terms must lead to an effective interaction which is anisotropic and, being density-dependent, depends on the ionic positions. To simplify our model, however, we shall represent the ion-ion, as well as the ion-electron, interaction by isotropic local potentials which do not depend on electron density. In his treatment, Evans[8, 17] took this density dependence into account. However, each ion was associated with electron density of equal and opposite charge, and the full electronic energy could be written as $\Sigma F_1$. This would be inconvenient in treating an external electric field (representing the effect of the electrolyte), which changes the number of electrons for a fixed number of ions.

An external electric field will give rise to a term in the electronic Hamiltonian and hence in the density functional, as well as to a potential for the ions. Including the former in $F_0$ and the latter in $F_1$, we have our partition function:

$$Q = \frac{1}{N!}\left(\frac{2\pi M}{\beta h^2}\right)^{3N/2} \int \mathrm{d}\Gamma \exp\left\{-\beta\left[F_0(n(\Gamma)) + \sum_i F_1(n(\Gamma), \mathbf{R}_i) + \sum_{ij}{}' F_2(\mathbf{R}_i, \mathbf{R}_j)\right]\right\} \tag{4}$$

In (4), we have made explicit the fact that, in the present level of approximation, the interionic interaction is by pairs. (The prime on the summation indicates it includes only distinct pairs.) Thus we will not treat induction-type interactions, which are not pairwise additive.

In addition to an interionic potential, we need an assumption for the interionic correlations. We will suppose that the probability of finding simultaneously an ion $i$ at $\mathbf{R}_1$ and an ion $j$ at $\mathbf{R}_2$ may be written

$$\rho^{(2)}(\mathbf{R}_1\mathbf{R}_2) = \rho^{(1)}(\mathbf{R}_1)\rho^{(2)}(\mathbf{R}_2)g(\mathbf{R}_1, \mathbf{R}_2) \tag{5}$$

with $\rho^{(1)}(\mathbf{R}_2)$ giving the probability of finding an ion at $\mathbf{R}_1$ and $g$ the radial distribution function corresponding to a homogeneous fluid.

## II DENSITY FUNCTIONAL THEORY

The electronic energy will be written as a functional of the electronic density. In addition to the pseudopotential interaction with the ion cores, it includes the commonly-used expressions[18,19] for kinetic energy, exchange energy, correlation energy, inhomogeneity energy, and interelectronic repulsion. In atomic units, which we shall be using from this point,

$$\begin{aligned} F_0(n(\Gamma)) = {} & \kappa_k \int n^{5/3}\, \mathrm{d}\tau - \kappa_a \int n^{4/3}\, \mathrm{d}\tau \\ & - \frac{1}{2}\int (0.115 - 0.031 \ln r_s)n\, \mathrm{d}\tau + \left(\frac{\lambda}{8}\right)\int n^{-1}(\nabla n)^2\, \mathrm{d}\tau \\ & + \frac{1}{2}\iint n(\mathbf{r})n(\mathbf{r}')|\mathbf{r} - \mathbf{r}'|^{-1}\, \mathrm{d}\tau\, \mathrm{d}\tau' \end{aligned}$$

The unit of energy is 27,2096 eV, the unit of length the Bohr radius $\alpha_0 = 0.5292 \times 10^{-8}$ cm, and $\hbar = e = m_e = 1$. In Eq. 6, $\kappa_k = \frac{3}{10}(3\pi^2)^{2/3}$. $\kappa_a = \frac{3}{4}(3/\pi)^{1/3}$, $r_s = (3/4\pi n)^{1/3}$, and $\lambda = \frac{1}{9}$. Although not all the terms in $F_0$ can be considered as definitely established, theories using them to describe the behaviour of conduction electrons at a surface have been quite successful.[19]

The inhomogeneity term, in $(\nabla n)^2$, represents the first term of the density-gradient expansion of the kinetic energy functional. Comparing exact results for the linear potential model with results obtained from the gradient expansion, Ma and Sahni[20] concluded that the expansion converges well, but that the second-gradient term is required if good results are to be obtained for all electron densities corresponding to metals. To obtain good results using only the first-gradient term, one can use a value for $\lambda$ greater than $\frac{1}{9}$; values of $\lambda$ are given[20] as a function of electron density. Sahni and Gruenbaum,[21] in variational calculations of the electron density for solid metal surfaces, incorporated the exact results from the linear potential calculations and investigated several methods of approximating the kinetic energy functional. They concluded that the gradient expansion worked as well as other methods in producing agreement of measureable properties with experiment. The ion-electron pseudopotential was the Ashcroft form, and was found to be satisfactory. Alonso and Girafalco[22] have stated that one cannot reproduce density oscillations, such as the Friedel oscillations, by minimizing a functional with respect to electron density, as long as only a finite number of terms in the gradient expansion are used for the kinetic energy. A non-local approximation to exchange was discussed and used to discuss local-density approximations.

In principle, the electron density for each ionic configuration $\Gamma$ could be determined by minimizing the electronic energy $E_0(n) = F_0(n) + \sum_i F_1(n, \mathbf{R}_i)$ with respect to $n$. If the electron density profile function $n$ involves one or more parameters $\alpha_k$, we would demand

$$\frac{\partial E_0}{\partial \alpha_k} = 0, \text{ all } k \tag{7}$$

with the normalization condition

$$\int n \, \mathrm{d}\tau = \text{constant} \tag{8}$$

Condition (8) may imply a relation between the $\{\alpha_k\}$, or it may be a consequence, independent of $\alpha_k$, of the form of the function.

The thermodynamic and electrical properties which interest us will always be given by an integral over ionic configurations. In such an integral, it is reasonable to expect that configurations differing substantially from the average will not contribute much. Thus, we will only consider choosing the best electronic distribution for the average ionic configuration. This means that for (7) we substitute

$$\frac{\partial \langle E_0 \rangle}{\partial \alpha_k} = 0, \text{ all } k \tag{9}$$

where the brackets refer to an average of $E_0$ over ionic configurations.

We will consider a large surface of planar symmetry, enclosed between the planes $z = -L$ (interior of the metal) and $z = L$ (exterior), and with a transverse area $A$ (Figure 1). The system contains $N$ ions of valence $q$ and hence of charge $qe$, where $e = 1.602 \times 10^{-19}$ C, and a number of electrons, equal to $Nq$ in the case of no external field. In the presence of an external field, the number of electrons will differ from $Nq$ to provide screening of the external field.

Within the system there is a surface region, so that the intensive properties pass from those of the homogeneous metal in the region near $z = -L$, to those of the vapor near $z = L$. The vapor density is neglected, and the electronic and ionic densities for the homogeneous metal are given by $n_e$ and $n_e/q$ respectively. We will assume that $L$ is sufficiently large so that the one-particle ionic distribution $\rho^{(1)}(z)$ approaches $n_e/q$ for $z = -L$ and 0 for $z = L$, while the electron density approaches $n_e$ for $z = -L$ and 0 for $z = L$; the electric charge density vanishes both at $z = -L$ and $z = L$. The total electric field is to be equal to the external field, if any, for $z = L$, and is to vanish at $z = -L$ (perfect screening).

In terms of the one-particle distribution, the total number of ions is:

$$N = A \int_{-L}^{L} \rho^{(1)}(z)\mathrm{d}z \tag{10}$$

while the number of electrons is

$$n_T = A \int_{-L}^{L} n(z)\mathrm{d}z \tag{11}$$

This means that

$$(Nq - n_T)e = \varepsilon_0 E^0 A \tag{12}$$

where $E^0$ is the external field.

The ionic density profile or average ionic configuration will be taken to be of the exponential form

$$\rho^{(1)}(z) = \frac{n_e}{q}[1 - \tfrac{1}{2}e^{\lambda(z-Y)}],\ z < Y \tag{13}$$

$$= \frac{n_e}{q}\tfrac{1}{2}e^{-\lambda(z-Y)},\ z \geq Y$$

The position of the ionic surface is represented by $Y$. Such a non-oscillatory profile is consistent with the consensus of theory and experiment for most liquid surfaces. On the other hand, use of a similar form

$$n(z) = n_e[1 - \tfrac{1}{2}e^{\alpha(z-x)}],\ z < X$$

$$= n_e\tfrac{1}{2}^{-\alpha(z-X)},\ z \geq X \tag{14}$$

for the electrons leaves out the Friedel oscillations in the electronic density. We might include oscillations by modifying $n(z)$ for $z < X$ so that

$$n = n_e[1 - \tfrac{1}{2}e^{\alpha(z-X)}\cos\beta(z - X)],\ z < X$$

$$= n_e[\tfrac{1}{2}e^{-\alpha(z-X)}],\ z \geq X \tag{15}$$

where the parameter $\beta$, like $\alpha$, is to be chosen to minimize the electronic energy according to the density functional theory. The calculations are more complicated than if $\beta = 0$, but most integrals can be ecaluated analytically. Theoretically, $\beta$ should be twice the Fermi momentum, or

$$\beta_{\text{theor}} = 2(3\pi^2 n_e)^{1/3} \tag{16}$$

However, the exponential decay of the amplitude of the oscillations with distance away from the surface is not in agreement with the actual behaviour (decaying as the inverse square).[19]

With the forms (13) and (15), and $X + L$ and $Y + L$ large, we have simply $An_e(Y + L)q^{-1}$ for the number of ions $N$ and $An_e[X + L + \beta^2/2\alpha(\alpha^2 + \beta^2)]$ for $n_T$, the number of electrons in the system. Therefore the external field determines the position of the electronic surface relative to the ionic according to (see Eq. 12):

$$(Y + L) - \left[X + L + \frac{\beta^2}{2\alpha(\alpha^2 + \beta^2)}\right] = \frac{\varepsilon_0 E^0}{n_e} \tag{17}$$

We consider $\beta$ as a variational parameter, whose effect is studied to investigate the sensitivity of our results to the form of the electron density profile. The calculations of surface energy for $\beta \neq 0$, presented in the Appendix, show no large changes compared to $\beta = 0$. This indicates our choice of electron density profile is not a major source of error. We put $\beta = 0$ for the rest of the calculations presented in the body of this article.

While the parameter(s) in the electron density profile are to be determined by minimization of the electronic energy, the single parameter $\lambda$ in the ionic density profile is not determined by our model. Evans and Kumaravadivel,[17,23] using an exponential density profile and a local quasithermodynamic approach their liquid metal theory, suggested minimization of the Helmholtz free energy per unit area for this purpose. For their system of non-correlated point ions, Allen and Rice [7a] minimized the surface energy to obtain the density profile, which they found to be oscillatory.

## III SURFACE TENSION AND SURFACE ENERGY

In our thermodynamic theory, the independent variables are $N$ (number of ions), $T$ (temperature), $V$ (volume), $A$, and the electrical variables. The number of electrons is determined by (12) in terms of the other parameters.

The excess superficial energy which we refer to, following common usage, as the surface energy, is the energy required to create an area $A$ of surface by separation of a volume of homogeneous metal into two parts. The relation between this quantity and the surface energy obtained by application of the Gibbs–Helmholtz equation to the surface tension will be discussed below.

We consider the case of no external field. As reference system, we imagine a cylindrical volume of area $(\frac{1}{2})A$ and length $2(Y + L)$, containing ions at a density $n_e/q$ and electrons at a density $n_e$. Separation of this system into two creates two surfaces, with total free surface area $A$. The difference between the new energy and that of the reference system is $U^s A$, where $U^s$ is the surface energy.

The electrostatic energy of the reference system, which is electrically neutral at each point, is zero. Thus $U^s A$ includes: the excess kinetic, exchange and correlation energies of the electrons; the total energy of inhomogeneity and electrostatic interaction; and the excess pseudopotential and exclusion energies. We have then

$$\begin{aligned} U^s = & \int_{-L}^{L} \mathrm{d}z[\tilde{f}(n) - \tilde{f}(n_e)\theta(Y - z)] \\ & + \frac{1}{2}\int_{-L}^{L} \mathrm{d}z \int \mathrm{d}\mathbf{r}[n(z) - q\rho^{(1)}(z)][n(z') - q\rho^{(1)}(z')]|\mathbf{r} - \mathbf{r}'|^{-1} \\ & + \int_{-L}^{L} \mathrm{d}z \int \mathrm{d}\mathbf{r}'\left[n(z)\rho^{(1)}(z) - \frac{n_e\theta(Y - z)n_e}{q}\right]\theta(R_c - |\mathbf{r} - \mathbf{r}'|)q|\mathbf{r} - \mathbf{r}'|^{-1} \\ & - \frac{q^2}{2}\int_{-L}^{L} \mathrm{d}z \int \mathrm{d}\mathbf{r}'\left[\rho^{(1)}(z)\rho^{(1)}(z') - \left(\frac{n_e}{q}\right)^2\theta(Y - z)\right] \\ & \times [1 - g(|\mathbf{r} - \mathbf{r}'|)]|\mathbf{r} - \mathbf{r}'|^{-1} \end{aligned} \tag{18}$$

Here, $\theta$ is the unit step function and the functional of the electron density

$$\tilde{f}(n) = \kappa_k n^{5/3} - \kappa_a n^{4/3} - \frac{1}{2}\left[0.115n - 0.031\ \ln\left(\frac{3}{4\pi n}\right)^{1/2}\right] + \frac{(\nabla n)^2}{72n} \tag{19}$$

where $n(z)$ is for the average ionic configuration. The simplest assumption for the correlation function, $g(r) = 1 - \theta(\mathrm{d} - r)$, gives

$$\begin{aligned} U^s = & \int_{-L}^{L} \mathrm{d}z[\tilde{f}(n) - \tilde{f}(n_e)\theta(Y - z)] \\ & + \frac{1}{2}\int_{-L}^{L} \mathrm{d}z \int \mathrm{d}\mathbf{r}'[n(z) - q\rho^{(1)}(z)][n(z') - q\rho^{(1)}(z')]|\mathbf{r} - \mathbf{r}|^{-1} \\ & + \int_{-L}^{L} \mathrm{d}z \int \mathrm{d}\mathbf{r}'[qn(z)\rho^{(1)}(z') - n_e^2\theta(Y - z)\theta(R_c - |\mathbf{r} - \mathbf{r}'|)|\mathbf{r} - \mathbf{r}'|^{-1} \\ & - \frac{1}{2}\int_{-L}^{L} \mathrm{d}z \int \mathrm{d}\mathbf{r}'[q_2\rho^{(1)}(z)\rho^{(1)}(z') - n_e^2\theta(Y - z)]\theta(d - |\mathbf{r} - \mathbf{r}|)|\mathbf{r} - \mathbf{r}'|^{-1} \end{aligned} \tag{20}$$

The surface tension $\gamma$ is obtained by differentiating the Helmholtz free energy with respect to the area of the system, keeping all other external parameters constant:

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{N,V,T,V^0,E^0} = -kT\left(\frac{\partial \ln Q}{\partial A}\right)_{N,V,T,V^0,E^0} \tag{21}$$

Only the configurational integral depends on $A$ at constant $N$ and $T$, so that

$$\gamma = -\frac{\beta^{-1}\partial(\int \mathrm{d}\Gamma e^{-\beta E})/\partial A}{\int \mathrm{d}\Gamma e^{-\beta E}} \tag{22}$$

where $E = F_0(n) + \Sigma F_1(n, \mathbf{R}_i) + \Sigma F_2(R_{ij})$. The surface energy $U_s$ could be defined by the Gibbs–Helmholz equation:

$$U_s = \gamma - T\left(\frac{\mathrm{d}\gamma}{\mathrm{d}T}\right) = \frac{\partial(\beta\gamma)}{\partial\beta} \tag{23}$$

Since the total energy $U$ is $\partial(\beta F)/\partial\beta$, we have also that

$$U_s = \left(\frac{\partial U}{\partial A}\right)_{N,V,T,V^0,E^0} \tag{24}$$

We shall show below that $U_s$ of Eq. 24 and $U_s$ of Eq. 18 are identical.

The electron density depends on the ionic configuration $\Gamma$ through the variational parameters which are chosen to minimize $E$ for each ionic configuration, according to Eq. (9). The $F_2$ terms, being independent of the electron density, would not enter. Let $F_0(n)$ be written as an integral over the volume of a functional $f(n)$, and $F_1(n, \mathbf{R}_i)$ as the integral of $n$ times $V(|\mathbf{r} - R_i|)$. Then the variational problem is

$$\int \mathrm{d}\tau \frac{\partial f}{\delta n}\frac{\partial n}{\partial \alpha_k} + \int \mathrm{d}\tau \sum_i V(|\mathbf{r} - \mathbf{R}_i|)\frac{\partial n}{\partial \alpha_k} = 0 \tag{25}$$

Note that $f$ differs from $\bar{f}$ of (19) by including the interelectronic repulsion.

In obtaining the expression for the surface tension, we use Green's scaled-coordinate method to carry out the differentiation in (22). The coordinates of each ion are written:

$$X_i = \sqrt{A}\xi_i \quad Y_i = \sqrt{A}\eta_i \quad Z_i + L = V\zeta_i A^{-1} \tag{26}$$

where $\xi_i$, $\eta_i$, and $\zeta_i$ are to be maintained constant during the differentiation with respect to $A$. Using asterisks to represent functions of scaled coordinates,

$$\gamma = \int e^{-\beta E^*}\left(\frac{\partial E^*}{\partial A}\right)\frac{\mathrm{d}\Gamma^*}{\int e^{-\beta E^*}\mathrm{d}\Gamma^*} \tag{27}$$

The two-body terms are like those appearing in the usual theories of surface tension:

$$\begin{aligned}\frac{\partial F_2^*(R_{ij})}{\partial A} &= F_2'(R_{ij})\left[\frac{\partial R_{ij}}{\partial X_i}\frac{X_i}{2A} + \frac{\partial R_{ij}}{\partial Y_i}\frac{Y_i}{2A} - \frac{\partial R_{ij}}{\partial Z_i}\frac{(Z_i + L)}{A}\right.\\ &\qquad\left. + \frac{\partial R_{ij}}{\partial X_j}\frac{X_j}{2A} + \frac{\partial R_{ij}}{\partial Y_j}\frac{Y_j}{2A} - \frac{\partial R_{ij}}{\partial Z_j}\frac{(Z_j + L)}{A}\right]\\ &= \frac{F_2'(R_{ij})}{A}\left[\frac{(X_i - X_j)^2 + (Y_i - Y_j)^2 - 2(Z_i - Z_j)^2}{2R_{ij}}\right] \qquad (28)\end{aligned}$$

The remaining terms in $(\partial E^*/\partial A)$ involve the electrons and are considered together.

We have to take into account that $n$ depends on $A$ through the variational parameters $\alpha_k$, which depend on ionic configuration, as well as through the normalization condition (12). The region of integration for electrons also changes, so we put $x = \sqrt{A}\xi$, $y = \sqrt{A}\eta$, and $z + L = V\zeta A^{-1}$, just as in Eq. 26.

$$\begin{aligned}\frac{\partial}{\partial A}\left[F_0^* + \sum_i F_1^*(n, \mathbf{R}_i)\right] &= \int \mathrm{d}\tau\left[\frac{\delta f}{\delta n}\frac{\partial n}{\partial A}\sum_i V(|\mathbf{r} - \mathbf{R}_i|) + n\sum_i \frac{\partial V(|\mathbf{r} - \mathbf{R}_i|)^*}{\partial A}\right.\\ &\qquad\left. + \frac{1}{2}\int \mathrm{d}\tau' n(\mathbf{r})n(\mathbf{r}')\frac{\partial|\mathbf{r} - \mathbf{r}'|^{-1}}{\partial A}\right] \qquad (29)\end{aligned}$$

The next-to-last term is simply

$$\begin{aligned}&\int \mathrm{d}\tau n\sum_i V'\left[\frac{\partial|\mathbf{r} - \mathbf{R}_i|}{\partial x}\frac{\partial x}{\partial A} + \frac{\partial|\mathbf{r} - \mathbf{R}_i|}{\partial X_i}\frac{\partial X_i}{\partial A}\cdots\right]\\ &= \sum_i \int \mathrm{d}\tau n V'(|\mathbf{r} - \mathbf{R}_i|)\frac{[(x - X_i)^2 + (y - Y_i)^2 - 2(z - Z_i)^2]}{2|\mathbf{r} - \mathbf{R}_i|A} \qquad (30)\end{aligned}$$

analogously to (28) and the last term in (29) is treated similarly. The change of $n$ with $A$ ($V$, $E^0$ constant) becomes (where $p$ is the parameter assuring normalization)

$$\begin{aligned}\frac{\partial n}{\partial A} &= \frac{\partial n}{\partial x}\frac{\partial x}{\partial A} + \frac{\partial n}{\partial y}\frac{\partial y}{\partial A} + \frac{\partial n}{\partial z}\frac{\partial z}{\partial A} + \frac{\partial n}{\partial p}\frac{\partial p}{\partial A} + \sum_k \frac{\partial n}{\partial \alpha_k}\frac{\partial \alpha_k}{\partial A}\\ &= \frac{\partial n}{\partial x}\frac{x}{2A} + \frac{\partial n}{\partial y}\frac{2}{2A} - \frac{\partial n}{\partial z}\frac{z + L}{A} + \frac{\partial n}{\partial p}\frac{\partial p}{\partial A}\\ &\quad + \sum_k \frac{\partial n}{\partial \alpha_k}\sum_k\left(\frac{\partial \alpha_k}{\partial X_j}\frac{X_j}{2A} + \frac{\partial \alpha_k}{\partial Y_j}\frac{Y_j}{2A} - \frac{\partial \alpha_k}{\partial Z_j}\frac{(Z_j + L)}{A}\right) \qquad (31)\end{aligned}$$

The last group of terms ($\sum_k \sum_j$), inserted in the integral of Eq. (29), makes no contribution by virtue of Eq. (25). Therefore,

$$\begin{aligned}
\left(\frac{\partial E^*}{\partial A}\right)_{N,V,T,E} &= \sum_{i<j} F_2'(R_{ij}) \frac{(X_i - X_j)^2 - 2(Z_i - Z_j)^2 + (Y_i - Y_j)^2}{2AR_{ij}} \\
&+ \sum_i \int \mathrm{d}\tau n V'(|\mathbf{r} - \mathbf{R}_i|) \frac{(x - X_i)^2 + (y - Y_i)^2 - 2(z - Z_i)^2}{2A|\mathbf{r} - \mathbf{R}_i|} \\
&- \int \mathrm{d}\tau n(\mathbf{r}) \int \mathrm{d}\tau' n(\mathbf{r}') \frac{(x - x')^2 - (z - z')^2}{2|\mathbf{r} - \mathbf{r}'|^3 A} + \int \mathrm{d}\tau \biggl( \frac{\delta f}{\delta n} \\
&+ \sum_i V(|\mathbf{r} - \mathbf{R}_i|) \biggr) \biggl( \frac{\partial n}{\partial x} \frac{x}{2A} + \frac{\partial n}{\partial y} \frac{y}{2A} - \frac{\partial n}{\partial z} \frac{z + L}{A} + \frac{\partial n}{\partial p} \frac{\partial p}{\partial A} \biggr)
\end{aligned} \tag{32}$$

which is inserted into (27).

On averaging over ionic configurations, the $x$ and $y$ directions become equivalent and the two-particle ionic distribution $\rho^{(2)}$ enters the first group of terms. In the second, we assume that we can substitute, for the true $n$ (parametrically dependent on ionic configuration), the electron density corresponding to the average ionic configuration, which we denote for now by $\bar{n}$. The averaging over $\Gamma$ then introduces the one-particle ionic distribution $\rho^{(1)}$, and, in the last group of terms, $\partial n/\partial x$ and $\partial n/\partial y$ can be dropped. Our surface tension now becomes

$$\begin{aligned}
\gamma = A^{-1} \biggl[ &\frac{1}{2} \int \mathrm{d}\mathbf{R}_1 \, \mathrm{d}\mathbf{R}_2 \, \rho^{(2)}(\mathbf{R}_1 \mathbf{R}_2) F_2'(R_{12}) R_{12}^{-1} (X_{12}^2 - Z_{12}^2) \\
&+ \int \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{R}_1 \bar{n}(\mathbf{r}) \biggl[ \rho^{(1)}(\mathbf{R}_1) V'(|\mathbf{r} - \mathbf{R}_1|) \frac{(x - X_1)^2 - (z - Z_1)^2}{A|\mathbf{r} - \mathbf{R}_1|} \\
&- \bar{n}(\mathbf{R}_1) \frac{(x - X_1)^2 - (z - Z_1)^2}{2A|\mathbf{r} - \mathbf{R}_1|^3} \biggr] + \int \mathrm{d}\mathbf{r} \biggl[ \frac{\delta f}{\delta \bar{n}} \\
&+ \int \mathrm{d}\mathbf{R}_1 \rho^{(1)}(\mathbf{R}_1) V(|\mathbf{r} - \mathbf{R}_2|) \biggr] \biggl( - \frac{\partial \bar{n}}{\partial z} \frac{z + L}{A} + \frac{\partial \bar{n}}{\partial p} \frac{\partial p}{\partial A} \biggr)
\end{aligned} \tag{33}$$

We now consider the effect of normalization. The value of $p$ is chosen to ensure

$$-A^{-1} \int \mathrm{d}\tau \bar{n} = - \int_{-L}^{L} \mathrm{d}z \bar{n}(z) = - \frac{n_T}{\mathrm{A}} = \varepsilon_0 E^0 - \frac{Nq}{A} \tag{34}$$

so that, with $E^0$ and $N$ constant,

$$\int_{-L}^{L} \mathrm{d}z \sum_k \left( \frac{\partial \bar{n}}{\partial \alpha_k} \frac{\partial \alpha_k}{\partial A} \right) + \int_{-L}^{L} \mathrm{d}z \left( \frac{\partial \bar{n}}{\partial p} \right) \left( \frac{\partial p}{\partial A} \right) = - \frac{Nq}{A^2} \tag{35}$$

Now suppose that $p$ is a parameter which shifts the surface density profile, such as $X$ in Eq. (15), so that $\partial\bar{n}/\partial p$ is $-\partial\bar{n}/\partial z$. Referring to the first group of terms as $T$, Eq. (36) becomes:

$$\left(\frac{\partial p}{\partial A}\right)_{N,V,E^0} = (T + NqA^{-2})\bigg/\int_{-L}^{L} \mathrm{d}z\left(\frac{\partial \bar{n}}{\partial z}\right) = -\frac{(T + NqA^{-2})}{n_e}$$

$$= \frac{T}{n_e} - \frac{(Y + L)}{A} \tag{36}$$

The terms $T$, inserted in (29), make no contribution by virtue of (25). Separating the functional $f$ into $\tilde{f}$ and the interelectron repulsion, we have from (33)

$$\gamma = \frac{1}{2}\int_{-L}^{L} \mathrm{d}z_1 \int \mathrm{d}\mathbf{R}_2 \Big[\rho^{(2)}(\mathbf{R}_1\mathbf{R}_2)F_2'(R_{12}) + 2n(\mathbf{R}_1)\rho^{(1)}(\mathbf{R}_2)V'(R_{12})$$
$$- n(\mathbf{R}_1)n(\mathbf{R}_2)R_{12}^{-2}\Big]\frac{X_{12}^2 - Z_{12}^2}{R_{12}} - \int \mathrm{d}\mathbf{r}\,\frac{\partial \tilde{f}}{\partial z}\,\frac{z + L - (Y + L)}{A}$$
$$- \int \mathrm{d}\mathbf{R}_1 \int \mathrm{d}\mathbf{R}_2\, \frac{\partial n(\mathbf{R}_1)}{\partial n_1}\, n(\mathbf{R}_2)\,\frac{Z_1 - Y}{AR_{12}}$$
$$- \int \mathrm{d}\mathbf{R}_1\, \mathrm{d}\mathbf{R}_2\, \frac{\partial n(\mathbf{R}_1)}{\partial Z_1}\,\rho^{(1)}(\mathbf{R}_2)V(R_{12})\,\frac{Z_1 - Y}{A} \tag{37}$$

The expression for the surface tension, Eq. (37), was obtained from the definition of $\gamma$ as the derivative of the free energy of the system with surface area, keeping the volume, the number of ions, and the external electric field constant. Using Euler's theorem for the surface system (Figure 1), we have for its free energy

$$F = \mu N - pV + \gamma A.$$

Now we consider, analogously to the excess superficial energy defined at the beginning of Section III, the difference between the free energy of the system containing the surface and the free energy of a reference system. The reference system, of the same total area and volume as the surface system, contains homogeneous liquid metal from $z = -L$ to $z = Y$, and homogeneous vapor from $z = Y$ to $z = L$. Using Euler's theorem for the homogeneous phases, we have

$$F^s = F - (F^m + F^v) = \mu N - pV + \gamma A - (\mu N^m + pV^m + \mu N^v + pV^v) \tag{38}$$

Here, $m$ = metal, $v$ = vapor; pressure $p$ and chemical potential $\mu$ are the same for all phases. Thus

$$F^s = \mu(N - N^m - N^v) + \gamma A \tag{39}$$

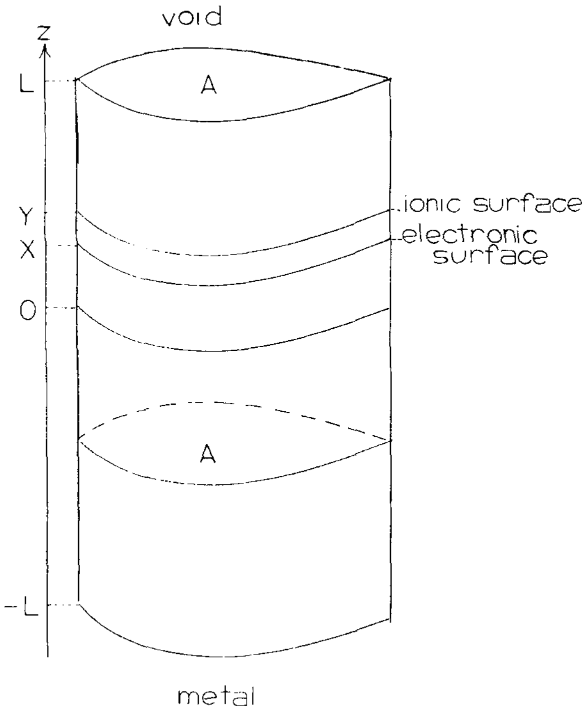

FIGURE 1

Since $F$ and the free energies of the homogeneous phases obey the Gibbs–Helmholtz equation,

$$\frac{\partial}{\partial T}\left(\frac{F^s}{T}\right)_{V,A} = -\frac{U}{T^2} + \frac{U^m + U^v}{T^2} \tag{40}$$

According to (39), $F^s$ is equal to $\gamma A$ if the dividing surface $z = Z$ is chosen so that $N^m + N^v$ is equal to $N$, i.e.

$$N = A(Z + L)n_e + A(L - Z)n_v$$

where $n_v$ is the ionic density in the vapor, which is neglected in our model. This is the choice made in our previous definition of $U^s$ (Eq. (18)). Therefore (40) yields

$$AU^s = A(U - U^m - U^v) = -T^2 \frac{\partial}{\partial T}\left(\frac{\gamma A}{T}\right) \tag{41}$$

or $U^s = \partial(\beta\gamma)/\partial\beta$, and we can identify $U^s$ with the surface energy obtained from the temperature dependence of the surface tension for zero external field.

## IV CALCULATION OF SURFACE PROPERTIES FOR METALS

For the purposes of calculation we further transform our expression (37) for the surface tension, to produce terms appearing in the expression for the surface energy, Eq. (20). In the first line of (37), we put:

$$\rho^{(2)}(\mathbf{R}_1\mathbf{R}_2) = \rho^{(1)}(Z_1)\rho^{(1)}(Z_2)g(R_{12}) \quad \text{and} \quad F_2' = -q^2R_{12}^{-2}.$$

This does not include the hard-sphere repulsion, which must be treated separately as follows:

$$\begin{aligned}\frac{1}{2}\int_{-L}^{L}\mathrm{d}Z_1 &\int \mathrm{d}\mathbf{R}_2\,\rho^{(1)}(Z_1)\rho^{(1)}(Z_2)e^{-W/kT}W'(R_{12})\,\frac{X_{12}^2 - Z_{12}^2}{R_{12}} \\ &= -\frac{kT}{2}\int_{-L}^{L}\mathrm{d}Z_1\rho^{(1)}(Z_1)\int \mathrm{d}\mathbf{R}_2\,\rho^{(1)}(Z_2)\left(\frac{\partial e^{-W/kT}}{\partial R_{12}}\right)\frac{R_{12}^2 - 3Z_{12}^2}{2R_{12}} \qquad (42)\end{aligned}$$

The exponential, which represents $g$, may be replaced by a step function, and its derivative by $\delta(R_{12} - d)$. After integrating the term in $f$ by parts, we obtain from (37)

$$\begin{aligned}\gamma = \frac{1}{2}\int_{-L}^{L}\mathrm{d}Z_1 &\int \mathrm{d}\mathbf{R}_2[n(Z_1) - q\rho^{(1)}(Z_1)][n(Z_2) - q\rho^{(1)}(Z_2)] \\ &\times [R_{12}^2 - 3X_{12}^2]R_{12}^{-3} + \frac{q^2}{2}\int_{-L}^{L}\mathrm{d}Z_1\rho^{(1)}(Z_1)\int \mathrm{d}\mathbf{R}_2\,\rho^{(1)}(Z_2)[1 - g(r_{12})] \\ &\times [X_{12}^2 - Z_{12}^2]R_{12}^{-3} - \frac{\pi kT}{2}\int_{-L}^{L}\mathrm{d}Z_1\rho^{(1)}(Z_1)\int_{|Z_{12}|}^{\infty}\delta(d - R_{12})\mathrm{d}R_{12} \\ &\times \int \mathrm{d}Z_{12}\,\rho^{(1)}(Z_{12} + Z_1)(R_{12}^2 - 3Z_{12}^2) + \int_{-L}^{L}\mathrm{d}Z_1\int \mathrm{d}\mathbf{R}_{12}\,n(Z_1)\rho^{(1)}(Z_2) \\ &\times \left[V + \frac{q}{R_{12}}\right]'[X_{12}^2 - Z_{12}^2]R_{12}^{-1} + (-L - Y)\tilde{f}(n_e) + \int \mathrm{d}Z_1\tilde{f}(n) \\ &+ \int \mathrm{d}Z_1\,\frac{\partial n(Z_1)}{\partial Z_1}\int \mathrm{d}\mathbf{R}_2\,\frac{Y - Z_1}{R_{12}}\,[n(Z_2) - q\rho^{(1)}(Z_2)] + \int \mathrm{d}Z_1\,\frac{\partial n(Z_1)}{\partial Z_1} \\ &\times \int \mathrm{d}\mathbf{R}_2(Y - Z_1)\rho^{(1)}(Z_2)\left[V + \frac{q}{R_{12}}\right] \qquad (43)\end{aligned}$$

The surface term from the integration by parts represents electrons in homogeneous metal ($z = -L$), which must be moved to the surface region as $A$ increases maintaining volume and electron number. Being independent of $\mathbf{r}_1$, it may be written as the integral in $Z_1$, over a length $Nq/n_eA$ (which equals $Y + L$), of the energy density for homogeneous electron gas.

Comparing the above equation with (20), we write the surface tension as:

$$\gamma = U^s - \frac{3}{2}\int_{-L}^{L} \mathrm{d}Z_1 \int \mathrm{d}R_2 [n(z_1) - q\rho^{(1)}(Z_1)][n(Z_2) - q\rho^{(1)}(Z_2)]\,\frac{X_{12}^2}{R_{12}^3}$$

$$+ \frac{3}{2}\int_{-L}^{L} \mathrm{d}Z_1 \int \mathrm{d}\mathbf{R}_2\, \theta(d - R_{12})[q^2\rho^{(1)}(Z_1)\rho^{(1)}(Z_2) - n_e^2\theta(Y - Z_1)]\,\frac{X_{12}^2}{R_{12}^3}$$

$$- \frac{\pi k T}{2}\int_{-L}^{L} \mathrm{d}Z_1 \rho^{(1)}(Z_1) \int_{-d}^{d} \mathrm{d}Z_{12}\, \rho^{(1)}(Z_{12} + Z_1)(d - 3Z_{12}^2)$$

$$+ \int_{-L}^{L} \mathrm{d}Z_1 \int \mathrm{d}\mathbf{R}_2\, n(Z_1)\rho^{(1)}(Z_2)\left[V + \frac{q}{R_{12}}\right]' \frac{[X_{12}^2 + (Z_2 - Z_1)(Y - Z_2)]}{R_{12}}$$

$$+ \int_{-L}^{L} \mathrm{d}Z_2 \left[\frac{\partial n(Z_1)}{\partial Z_1}\right] \int \mathrm{d}R_2 (Y - Z_1)[n(Z_2) - q\rho^{(1)}(Z_2)]R_{12}^{-1} \qquad (44)$$

where the prime means differentiation with respect to $R_{12}$. An integration by parts has been performed on the last term of (43).

To illustrate the use of the formulas we introduce the following assumptions, which constitute the simplest models of the class we have developed. (1) The empty-core pseudopotential makes $V = qR_{12}^{-1}\theta(R_{12} - R_c)$. (2) For $g$ we put $\theta(R_{12} - d)$ with $d$ the hard-sphere diameter. Then the terms in surface energy and surface tension may be labelled as electronic, electrostatic (Coulombic interactions between charged particles), exclusion (depending on $d$), and pseudopotential (depending on $R_c$). Inserting the profile of Eq. (13) for the ions and that of Eq. (14) for the electrons, we obtain the following expressions:

$$U_{\text{electron}}^s = \gamma_{\text{electron}} = -1.6423\,\frac{n_e^{5/3}}{\alpha} + 0.25037\,\frac{n_e^{4/3}}{\alpha} + 0.006584\,\frac{n_e}{\alpha} + n_e\alpha \ln 2/72 \qquad (45)$$

$$U_{\text{coulomb}}^s = \frac{\pi n_e^2}{2}\left[\frac{1}{\alpha^3} + \frac{1}{\lambda^3} - \frac{4}{\alpha\lambda(\alpha + \lambda)}\right] \qquad (46)$$

$$\gamma_{\text{coulomb}} = \pi n_e^2\left[\frac{1}{2\alpha^3} + \frac{2\lambda^3 - \alpha\lambda^2 + 2\alpha^2\lambda - \alpha^3}{\alpha\lambda^3(\alpha + \lambda)^2}\right] \qquad (47)$$

$$U_{\text{exclusion}}^s = \pi n_e^2\left[e^{-\lambda d}\left(\frac{5}{2\lambda^3} + \frac{d}{2\lambda^2}\right) + \frac{d^3}{6} + \frac{2d}{\lambda^2} - \frac{5}{2\lambda^3}\right] \qquad (48)$$

$$\gamma_{\text{exclusion}} = \pi n_e^2\left[e^{-\lambda d}\left(\frac{9}{\lambda^4 d} + \frac{4}{\lambda^3} + \frac{d}{2\lambda^2}\right) - \frac{9}{\lambda^4 d} + \frac{5}{\lambda^3} - \frac{d}{\lambda^2} + \frac{d^3}{24}\right]$$
$$- \pi kT\, n_e^2\left[e^{-\lambda d}\left(-\frac{d^3}{2\lambda} - \frac{7d^2}{2\lambda^2} + \frac{9d}{\lambda^3} - \frac{9}{\lambda^4}\right) + \frac{9}{\lambda^4} - \frac{d^2}{\lambda^2} + \frac{d^4}{8}\right] \tag{49}$$

$$U^s_{\text{pseudopot.}} = 2\pi n_e^2\left[\frac{e^{-\alpha R_c}}{\alpha}\left(\frac{1}{\alpha^2 - \lambda^2} - \frac{1}{\alpha^2}\right) + \frac{e^{-\lambda R_c}}{\lambda}\left(\frac{1}{\lambda^2 - \alpha^2} - \frac{1}{\lambda^2}\right)\right.$$
$$\left. + \frac{1}{\alpha^3} + \frac{1}{\lambda^3} + \frac{1}{\alpha\lambda(\alpha + \lambda)} - \frac{R_c}{\alpha^2} - \frac{R_c}{\lambda^2} - \frac{R_c^3}{6}\right] \tag{50}$$

$$\gamma_{\text{pseudopot.}} = 2\pi n_e^2\left[e^{-\alpha R_c}\left(\frac{1}{\alpha(\alpha^2 - \lambda^2)} - \frac{1}{\alpha^3} - \frac{2\alpha}{\lambda^2(\alpha^2 - \lambda^2)} + \frac{2}{\alpha\lambda^2}\right.\right.$$
$$\left. + \frac{2\alpha}{(\alpha^2 - \lambda^2)^2}\right) + e^{-\lambda R_c}\left(\frac{2}{\lambda^3} - \frac{1}{\lambda(\lambda^2 - \alpha^2)} + \frac{R_c}{\lambda^2} - \frac{R_c}{\lambda^2 - \alpha^2}\right.$$
$$\left. - \frac{\lambda^2 + \alpha^2}{\lambda(\lambda^2 - \alpha^2)^2}\right) - \frac{2}{\lambda^3} + \frac{1}{\alpha^3} - \frac{1}{2\alpha\lambda(\alpha + \lambda)} + \frac{2}{\lambda^2(\alpha + \lambda)}$$
$$\left. + \frac{1}{\lambda(\alpha + \lambda)^2} - \frac{2}{\alpha\lambda^2} - \frac{R_c}{\alpha^2} + \frac{R_c}{\lambda^2} - \frac{R_c^3}{6}\right] \tag{51}$$

The parameters in this simplest model are the following: the electron density $n_e$ (known experimentally), the "width parameters" $\lambda$ and $\alpha$ for the ionic and electronic density profiles, the pseudopotential core radius $R_c$, and the hard-sphere diameter $d$. The parameter $\alpha$ will be determined by variational calculations. The values of $R_c$ will be those given by other authors. As we now show, the parameter $d$ in the model may be determined, once $R_c$ is chosen, by demanding that the model give the proper pressure for the homogeneous system; or it may be put equal to the "vacuum" values $2R_c$.

We calculate the pressure according to

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N,E^0} = \frac{NkT}{V} - \frac{\int d\Gamma e^{-E/kT}(\partial E^*/\partial V)}{\int d\Gamma e^{-E/kT}} \tag{52}$$

where the asterisk refers to the use of scaled coordinates in the differentiation: $x = V^{1/3}\xi$, $y = V^{1/3}\eta$, etc. The electron density $n_e$ for the homogeneous system depends on $V$, since the constancy of $N$ requires

$$\frac{\partial n_e}{\partial V} = -\frac{n_e}{V}.$$

A calculation similar to that for the surface tension gives

$$
\begin{aligned}
\frac{\partial E^*}{\partial V} &= \frac{\partial}{\partial V}\left(\sum_{i<j} F(R_{ij})^* + \int \mathrm{d}\tau^* \tilde{f}(n)\right) \\
&\quad + \frac{\partial}{\partial V}\left(\int \mathrm{d}\tau\, \mathrm{d}\tau' \frac{n_e^2}{2} |r - r'|^{-1}\right)^* + \frac{\partial}{\partial V}\int \mathrm{d}\tau^* n_e \sum_i V(|\mathbf{r} - \mathbf{R}_i|)^* \\
&= \sum_{i<j} F'(R_{ij}) \frac{R_{ij}}{3V} + \frac{1}{V}\int \mathrm{d}\tau\left(\tilde{f}(n_e) - n_e \frac{\delta \tilde{f}}{\delta n_e}\right) \\
&\quad - \frac{n_e^2}{6V}\int \mathrm{d}\tau\, \mathrm{d}\tau' |\mathbf{R} - \mathbf{R}'|^{-1} + \int \mathrm{d}\tau n_e \sum_i V'(|\mathbf{r} - \mathbf{R}_i|) \frac{|\mathbf{r} - \mathbf{R}_i|}{3V}
\end{aligned}
$$

which leads to

$$
\begin{aligned}
p &= \frac{NkT}{V} - \frac{1}{3V}\int \mathrm{d}\mathbf{R}_1\, \mathrm{d}\mathbf{R}_2 \tfrac{1}{2}\rho^{(2)}(\mathbf{R}_1\mathbf{R}_2) F'(R_{12}) - \frac{1}{V}\int \mathrm{d}\mathbf{R}_1\left(\tilde{f} - n\frac{\delta \tilde{f}}{\delta n}\right)_e \\
&\quad + \frac{n_e^2}{6V}\int \mathrm{d}\mathbf{R}_1\, \mathrm{d}\mathbf{R}_2 |\mathbf{R}_1 - \mathbf{R}_2|^{-1} - \frac{1}{3V}\int \mathrm{d}\mathbf{R}_1 n_e \int \mathrm{d}\mathbf{R}_2\, \rho^{(1)}(\mathbf{R}_2) V'(R_{12}) R_{12} \\
&\quad - \frac{1}{2}\frac{n_e^2}{q^2}\int d\mathbf{R}_{12}\, e^{-W/kT}\left(\frac{\partial W}{\partial R_{12}}\right)\frac{X_{12}^2}{R_{12}} \\
&= \frac{NkT}{V} - \frac{n_e^2}{6V}\int \mathrm{d}\mathbf{R}_1\, \mathrm{d}\mathbf{R}_2\, R_{12}^{-1}\theta(d - R_{12}) - \frac{1}{V}\int \mathrm{d}\mathbf{R}_1\left(\tilde{f} - n\frac{\delta \tilde{f}}{\delta n}\right)_e \\
&\quad + \frac{n_e^2}{3V}\int \mathrm{d}\mathbf{R}_1\, \mathrm{d}\mathbf{R}_2 [\theta(R_c - R_{12}) R_{12}^{-1} + \delta(R_c - R_{12})] + \frac{2\pi n_e^2 kT}{3q^2} \\
&\quad \times \int_0^\infty \mathrm{d}R R^3 \left(\frac{\partial e^{-W/kT}}{\partial R}\right)
\end{aligned} \tag{53}
$$

For the simplest model,

$$
p = \frac{kTn_e}{q} - \frac{2\pi n_e^2 d^2}{6} - \tilde{f}(n_e) + n_e \frac{\partial \tilde{f}}{\delta n_e} + 2\pi n_e^2 R_c^2 + \frac{2\pi n_e^2}{3\beta q^2} d^3 \tag{54}
$$

with

$$
f(n_e) - n_e \frac{\partial \tilde{f}}{\delta n_e} = -\tfrac{2}{3}\kappa_k n_e^{5/3} + \tfrac{1}{3}\kappa_a n_e^{4/3} + \frac{0.031}{6} n_e
$$

The pressure $p$ in (54) is to be 1 atmosphere ($3.44 \times 10^{-9}$ a.u./$a_0^3$), which is negligible compared to the other terms since $n_e$ is several times $10^{-3}/a_0^3$, so that:

$$\frac{\pi d^2}{3} = \frac{kT}{qn_e} + \frac{1.9142}{n_e^{1/3}} - \frac{0.24619}{n_e^{2/3}} - \frac{0.005167}{n_e} + 2\pi R_c^2 + \frac{2\pi kTd^3}{2q^2} \qquad (55)$$

The last term being relatively unimportant, we may solve iteratively for $d$.

## V CALCULATIONS FOR THE ALKALI METALS

We illustrate use of the formulas for the alkali metals just above their melting points. The densities used are from a Table given by Beer.[24] Converted to ions per unit volume, they are given in Table I, along with the melting points and experimental surface tensions and surface energies. The pseudopotential core radii $R_c$, also given in Table I, are those used by Kumaravadivel and Evans,[8] and generally represent an average of the values used by others. Two values are considered for the hard sphere diameter: $d = 2R_c$, and $d$ chosen (Eq. (55)) to give the correct pressure in the homogeneous phase.

The procedure for determining the width parameter for the electronic distribution is as follows: for a given value of $\lambda$, the surface energy $U^s$ is computed with different values of $\alpha$, and the value which minimizes $U^s$ is taken. The surface tension $\gamma$ is computed for each value of $\lambda$, using the appropriate value of $\alpha$. We expect $\gamma$ to vanish for small $\lambda$ (infinitely broad surface region) and, as $\lambda$ increases, increase.

The results for Cs are given in Table II and Figure 2. We see that the proper behavior for $\lambda \to 0$ is found (provided that $\alpha$ is very carefully determined), as well as the maximum in $\gamma$, which is too small to appear on our graph. However, no minimum is found. The surface tension, which is quite unvarying from $\lambda = 1.5$ on, is half the experimental value and the surface energy a bit high. The difference between the two quantities, which is $T$ times the surface entropy, is much too large. The foregoing is when $d$ is chosen from the pressure in the homogeneous phase; the choice $d \approx 2R_c$, decreases $\gamma$ and $U^s$ by about 10 per cent.

For the metals of higher electron density, similar results are found (Table III), except that the maximum in $\gamma$, already faint for $Cs$, has disappeared by the time Li is reached. The errors in $\gamma$ and $U^s$ become more important: the calculated surface tension is about half the experimental value in all cases, while the ratio of calculated surface energy to experimental increases as $n_e$ increases. The increase in $\gamma$ and $U^s$ with electron density is correctly reproduced. If $d = 2R_c$ is used, however, the results become unacceptable; surface tensions decrease with increasing electron density, and negative surface tensions appear (Table IV). We note that (a) the model is about the simplest

TABLE I

Parameters for calculations

| Metal | Ion density, ions/$a_0^3$ [a] | Melting point, K[a] | $R_c/a_0$ [b] | $d/a_0$, from (55) | Surface Tens, dyn/cm[a] | Surface En, dyn/cm[a,c] |
|---|---|---|---|---|---|---|
| Lithium | $6.5973 \times 10^{-3}$ | 453.2 | 1.26 | 3.48858 | 398 | 461 |
| Sodium | $3.5944 \times 10^{-3}$ | 371.2 | 1.70 | 4.28706 | 191 | 228 |
| Potassium | $1.8782 \times 10^{-3}$ | 337.2 | 2.21 | 5.18557 | 115 | 142 |
| Rubidium | $1.5348 \times 10^{-3}$ | 312.2 | 2.61 | 6.07405 | 85 | 104 |
| Cesium | $1.2341 \times 10^{-3}$ | 302.2 | 2.00 | 4.18217 | 70 | 88 |

[a] S. Z. Beer, ed.: *Liquid Metals-Chemistry and Physics* (Marcel Dekker, New York, 1972), pp. 186–187.

[b] R. Kumarvaadivel and R. Evans, *J. Phys. C., Solid State Physics*, **8**, 793 (1975).

[c] Calculated as $\gamma - T(\mathrm{d}\gamma/\mathrm{d}T)$ from data in Ref. (a).

TABLE II

Surface properties for cesium

| | | Results for $d = 4.18217\ a_0^{-1}$ | | Results for $d = 2\ Rc$ | |
|---|---|---|---|---|---|
| $\lambda(a_0^{-1})$ | Best $\alpha$ | $\gamma$ (dyn/cm) | $U^s$ (dyn/cm) | (dyn/cm) | $U^s$ (dyn/cm) |
| 0.1 | 0.10029457 | 4.41 | 815.51 | 4.12 | 731.48 |
| 0.2 | 0.202199 | 8.87 | 416.65 | 8.28 | 373.51 |
| 0.4 | 0.41105 | 17.97 | 225.57 | 16.88 | 201.91 |
| 0.7 | 0.66686 | 28.99 | 153.87 | 27.36 | 137.52 |
| 1.0 | 0.78899 | 33.45 | 130.76 | 31.46 | 116.78 |
| 1.5 | 0.86233 | 35.25 | 116.65 | 32.92 | 104.10 |
| 2.0 | 0.88814 | 35.60 | 111.28 | 33.09 | 99.25 |
| 2.5 | 0.89985 | 35.67 | 108.71 | 33.07 | 96.92 |
| 3.0 | 0.90610 | 35.69 | 107.29 | 33.03 | 95.63 |
| 3.2 | 0.90780 | 35.69 | 106.89 | 33.02 | 95.27 |
| 3.4 | 0.90921 | 35.69 | 106.56 | 33.00 | 94.97 |
| 3.6 | 0.91037 | 35.68 | 106.29 | 32.99 | 94.72 |
| 4.0 | 0.91215 | 35.68 | 105.86 | 32.97 | 94.33 |
| 4.4 | 0.91351 | 35.67 | 105.53 | 32.95 | 94.04 |
| 5.0 | 0.91493 | 35.67 | 105.19 | 32.92 | 93.72 |
| 6.0 | 0.91644 | 35.66 | 104.82 | 32.90 | 93.39 |
| 7.0 | 0.91732 | 35.65 | 104.60 | 32.88 | 93.19 |
| 10.2 | 0.91859 | 35.64 | 104.30 | 32.86 | 92.91 |
| 13.0 | 0.91909 | 35.63 | 104.17 | 32.85 | 92.80 |
| 20.0 | 0.91947 | 35.63 | 104.07 | 32.84 | 92.71 |

possible of the type we consider and (b) $\gamma$ and $U^s$ are each a sum of a number of positive and negative contributions, some of which are larger than $\gamma$ and $U^s$ themselves. The breakdown is shown in Table V, with $\lambda = 4a_0^{-1}$, for all five metals. It is quite different from that of Allen and Rice [7a], who introduced an *ad hoc* "stabilization" potential to compensate for their use of point ions with no pseudopotential. The fact that $\gamma$ and $U^s$ change little as $\lambda$ increases past $2a_0^{-1}$ means that, when discussing the predictions of the model, we can take any $\lambda$ above $2a_0^{-1}$.

We may also calculate the difference of electrical potential between the inside and the outside of the metal, due to the difference between $\alpha$ and $\lambda$, which creates a dipole layer at the surface. An elementary calculation gives

$$V(\infty) - V(-\infty) = \frac{n_e e}{\varepsilon}(\lambda^{-2} - \alpha^{-2}) \qquad (56)$$

which makes the potential difference in volts $\Delta V = 341.71$ volts × $(\lambda^{-2} - \alpha^{-2})n_e$ when $n_e$, $\lambda$ and $\alpha$ are in atomic units. Potential differences

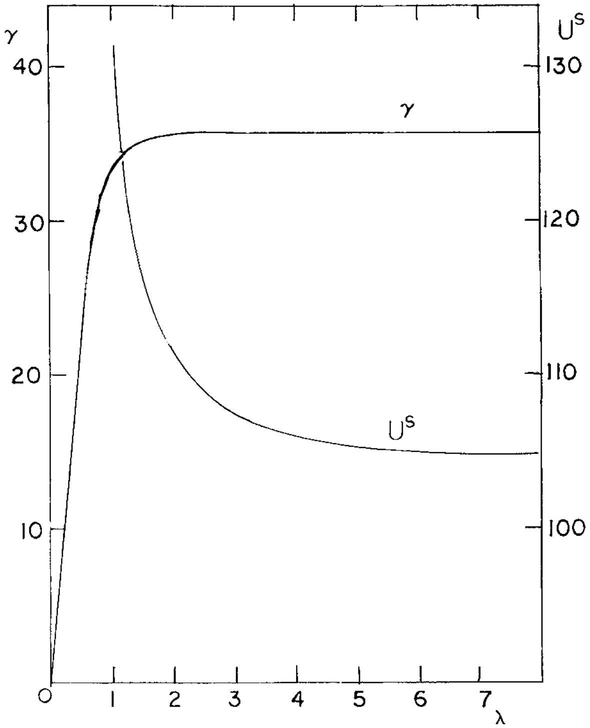

FIGURE 2

## TABLE III

Calculated results for surface properties, *d* computed from Pressure[a]

| | $\lambda = 2a_0^{-1}$ | | $\lambda = 3a_0^{-1}$ | | $\lambda = 4a_0^{-1}$ | |
|---|---|---|---|---|---|---|
| Metal | $\gamma$ | $U^s$ | $\gamma$ | $U^s$ | $\gamma$ | $U^s$ |
| Li | 141.4 | 1467.1 | 144.8 | 1368.1 | 146.3 | 1331.7 |
| Na | 95.0 | 790.9 | 96.5 | 753.9 | 97.0 | 740.5 |
| K | 56.1 | 381.9 | 56.7 | 369.5 | 56.8 | 365.1 |
| Rb | 48.6 | 391.7 | 49.0 | 381.9 | 49.2 | 378.4 |
| Cs | 35.6 | 111.3 | 35.7 | 107.3 | 35.7 | 105.9 |

[a] All results in dyn/cm.

TABLE IV

Calculated results for surface properties, $d = 2R_c$

| Metal | $\lambda = 2a_0^{-1}$ $\gamma$ | $\lambda = 2a_0^{-1}$ $U^s$ | $\lambda = 3a_0^{-1}$ $\gamma$ | $\lambda = 3a_0^{-1}$ $U^s$ | $\lambda = 4a_0^{-1}$ $\gamma$ | $\lambda = 4a_0^{-1}$ $U^s$ |
|---|---|---|---|---|---|---|
| Li | −50.0 | 426.3 | −65.6 | 383.9 | −72.3 | 367.5 |
| Na | 4.7 | 347.2 | 0.2 | 325.6 | −1.7 | 317.7 |
| K | 21.7 | 222.7 | 20.7 | 213.9 | 20.2 | 210.8 |
| Rb | 12.5 | 229.7 | 11.7 | 222.6 | 11.4 | 220.0 |
| Cs | 33.1 | 99.2 | 33.0 | 95.6 | 33.0 | 94.3 |

[a] All results in dyn/cm.

calculated in this way are shown in Table VI for the computations of Table IV: we again note the insensitivity to $\lambda$ in the range considered. Subtracting $\Delta V$ from the chemical potential of the electrons gives the work function. The chemical potential $\mu_e$ may be calculated as the derivative of the bulk electronic energy density with respect to the electron number density, which gives (see Eq. 6)

$$\begin{aligned}\mu_e &= \tfrac{5}{3}\kappa_k n_e^{2/3} - \tfrac{4}{3}\kappa_a n_e^{1/3} - 0.07007 - 0.005167 \ln n_e \\ &\quad + \int n_e |\mathbf{r} - \mathbf{r}'|^{-1}\, d\tau' - \int n_e |\mathbf{r} - \mathbf{r}'|^{-1} \theta(|\mathbf{r} - \mathbf{r}'| - R_c) d\tau' \\ &= 4.7854 n_e^{2/3} - 0.9847 n_e^{1/3} - 0.07007 - 0.005167 \ln n_e + 2\pi R_c^2 n_e \qquad (57)\end{aligned}$$

These results are also given in Table VI. Combining the surface and bulk contributions for $\lambda = 4a_0^{-1}$, we find electrochemical potentials (minus work functions) of −2.89, −2.48, −2.06, −1.93, and −1.93 volts for the metals from Li to Cs. Experimental values for polycrystalline samples are −3.1, −2.7, −2.4, −2.2, and −2.1 respectively,[25] although the values for liquid metals may be somewhat different. Our agreement is thus quite reasonable (note that the interionic potential and pair distributions enter only indirectly in calculation of this property). It is interesting that the variations in bulk and surface contributions to $\mu_e$, as one passes from Li to Cs, are larger than the variations in the sum.

## VI DISCUSSION

We have presented a simple formalism for the treatment of surface properties of metals, with a view toward investigating the effect of external electric fields and studying the metal's contribution to the electrochemical interface. In this formalism a density functional is used for the conduction electrons, while the ion cores are treated as actual particles, using pseudopotential

## TABLE V

Contributions to surface tension and surface energy (dyn/cm) with $\lambda = 4a_0^{-1}$ and variationally chosen $\alpha$

| | Contributions to $U^s$ and $\gamma$ | | | | Contributions to $U^s$ | | | Contributions to $\gamma$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Metal | Kinetic | Excha. | Inhom. | Correl. | Electro. | Exclusion | Pseudopot. | Electro. | Exclusion | Pseudopot. | Hard-core |
| Li | −703.8 | 572.1 | 83.3 | 80.2 | 153.3 | 1590.6 | −444.0 | 195.9 | 344.6 | −420.6 | −5.4 |
| Na | −286.2 | 284.8 | 40.6 | 48.9 | 65.5 | 861.1 | −274.2 | 80.3 | 195.0 | −263.3 | −3.1 |
| K | −104.8 | 129.5 | 19.6 | 27.6 | 22.9 | 411.4 | −141.2 | 27.4 | 95.9 | −136.8 | −1.6 |
| Rb | −85.3 | 112.7 | 14.1 | 25.7 | 23.1 | 438.5 | −150.4 | 26.6 | 104.0 | −146.8 | −1.0 |
| Cs | −39.8 | 56.6 | 16.9 | 13.9 | 4.1 | 94.4 | −40.2 | 5.4 | 21.3 | −3.8 | −0.3 |

TABLE VI

Electrochemical potentials

| Metal | $V(\infty) - V(-\infty)$, volts $\lambda = 2a_0^{-1}$ | $\lambda = 3a_0^{-1}$ | $\lambda = 4a_0^{-1}$ | Chemical (bulk), contribution (volts) |
|---|---|---|---|---|
| Li | −2.9791 | −3.0167 | −3.0317 | 0.1451 |
| Na | −2.0402 | −2.0737 | −2.0869 | −0.3883 |
| K | −1.2422 | −1.2696 | −1.2801 | −0.7794 |
| Rb | −1.3371 | −1.3578 | −1.3658 | −0.5663 |
| Cs | −0.4805 | −0.4668 | −0.4292 | −1.4970 |

theory to justify such an approach. We have given formulas for surface tension, surface energy, and electrical properties of the surface, and illustrated their use by performing calculations for the alkali metals using the simplest models. The cancellation between large terms that contribute to surface properties means, of course, that a change in the way any contribution is calculated can have a significant effect. However, using a more realistic assumption for the interionic correlation seems most important for several reasons. First, this is the largest term in $U^s$ and $\gamma$. Second, the work function, which does not involve $\rho^{(2)}$ and the interionic potential directly, comes out much more accurately than other properties. (In fact, we have studied the change in this quantity with external field using the present model, to show the contribution of the metal to double-layer capacitance.) As we mentioned in the Introduction, the interionic potential, even for the bulk metal, should have an oscillating part, but, even for the simple potential we have used, the step-function is quite a crude approximation for the correlation function, and should become worse as densities increase. Better correlation functions for bulk metal, like better potentials, are available. However, the ion-ion repulsion is the main determiner of the ionic arrangement in bulk liquid,[26] and Ashcroft and Lekner[16] showed that the correlation function for a hard-sphere model could be used, in conjunction with a good interionic potential, to produce good results for the resistivity. Indeed, we

TABLE VII

Effect of second parameter on energy

| $n_e(a_0^{-3})$ | $\lambda$ | Best $\alpha$ with $\beta = 0$ | Surface En. (dyn/cm) | Best $\alpha$ and $\beta$ | | Surface En. (dyn/cm) |
|---|---|---|---|---|---|---|
| 0.0012341 | 4.0 | 0.91215 | 105.86 | 0.8827 | 0.2751 | 105.82 |
| 0.0012341 | 2.0 | 0.88814 | 111.28 | 0.8580 | 0.2645 | 111.24 |
| 0.0012341 | 1.0 | 0.78899 | 130.76 | 0.7677 | 0.1421 | 130.75 |
| 0.0065973 | 4.0 | 0.84294 | 1331.69 | 0.7827 | 0.3140 | 1330.04 |
| 0.0065973 | 2.0 | 0.79771 | 1467.09 | 0.7130 | 0.3436 | 1462.54 |
| 0.0065973 | 1.0 | 0.64484 | 1910.41 | 0.5348 | 0.3766 | 1889.615 |

have used hard-sphere correlation functions to estimate the correction to be added to $U^s$, due to the changed $g(r)$, keeping the interionic interaction potential unchanged. We estimate corrections of $-13$ dyn/cm for Cs and $-600$ dyn/cm for Li, clearly of the right size. More detailed calculations are in progress.

Of course, use of bulk correlation functions to describe the surface is open to criticism, but other work seems to show the form (5) is not so bad for obtaining surface properties. The pseudo-ion theory of Evans and Kumaravadivel,[4,8] which obtained much better surface energies than we obtained for the alkali metals, used the assumption of Eq. (5), but with the experimental bulk liquid correlation function for $g$, and a more complicated, density-dependent interionic potential. (Other corrections were made as well.) Surface tensions could not be calculated in the context of this model, so the authors[17] turned to a thermodynamic perturbation theory, with further improvements in the two-particle distribution function. They determined the ion density profile by minimization of the free energy, and also found the ion-profile to be much sharper than the electron profile. However, in a Coulombic model such as ours, it is important to modify $g$ to take into account the electroneutrality constraint in the surface.[27]

The density functional used to describe the electron energy, as well as the electron-ion pseudopotential, could be changed, also without changing the basic structure of the model. In particular, a different correlation energy functional may be appropriate for liquid metal densities.[28] Of course, one should maintain consistency by assuring that the pressure is correctly calculated for the bulk liquid. Use of density-dependent potentials probably necessitates introduction of additional parameters, and would take us out of the formalism developed here. We believe that improvements in some of the terms can give $\gamma$ in good agreement with experiment, which would validate the use of this kind of model to describe polarization effects, such as are important in the charged electrochemical interface.

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## Appendix

In this appendix we show the effect of introducing oscillations into the electron density profile, by using the two-parameter form of Eq. (15). At the same time, we give explicit formulas for some of the terms entering the surface energy expression. In some cases, use of the identity

$$\cos \beta z = \tfrac{1}{2}(e^{i\beta z} + e^{-i\beta z})$$

allows easy deduction of expressions involving $\beta$ from expressions with only $\alpha$ (non-oscillating profile). All the expressions are independent of the sign of $\beta$, so that $\beta = 0$ must be a stationary value for the energy.

Since the electronic terms are not linear in $n(z)$, their calculation is not so simple. Using the binomial expansion, we find for the kinetic energy

$$\begin{aligned}\int_{-\infty}^{\infty} \kappa_k n^{5/3}\,\mathrm{d}z - \int_{-\infty}^{Y} \kappa_k n_e^{5/3} &= \kappa_k n_e^{5/3}\left\{\int_{-\infty}^{X} [1 - \tfrac{1}{2}e^{\alpha(z-X)} \cos \beta(z - X)]^{5/3}\,\mathrm{d}z\right. \\ &\quad \left. + \int_{X}^{\infty} [\tfrac{1}{2}e^{-\alpha(z-X)}]^{5/3}\,\mathrm{d}z - \int_{-\infty}^{Y} \mathrm{d}z\right\} \\ &= \kappa_k n_e^{5/3}\left[X - Y + \sum_{k=1}^{\infty} \frac{(\frac{5}{3})(\frac{2}{3})\cdots(\frac{5}{3} - k + 1)}{(-2)^k \beta}\, I_k\!\left(\frac{k\alpha}{\beta}\right) + \left(\frac{1}{2}\right)^{5/3}\left(\frac{3}{5\alpha}\right)\right] \qquad (58)\end{aligned}$$

where

$$I_k\left(\frac{k\alpha}{\beta}\right) = (k!)^{-1} \int_0^\infty e^{-k\alpha x/\beta} \cos k\alpha \, \mathrm{d}x \tag{59}$$

can be evaluated in closed form. For no external field, $X = \beta^2/2\alpha(\alpha^2 + \beta^2) + Y$. Similarly, the exchange energy is

$$\kappa_a n_e^{4/3}\left[X - Y + \sum_{k=1}^{\infty} \frac{(\frac{4}{3})(\frac{1}{3})\cdots(\frac{4}{3} - k + 1)}{(-2)^k\beta} I_k\left(\frac{k\alpha}{\beta}\right) + \left(\frac{1}{2}\right)^{4/3}\left(\frac{3}{4\alpha}\right)\right]$$

and the correlation energy, after some algebra, is

$$= -\tfrac{1}{2}\left[(0.129801n_e + 0.010333n_e \ln n_e)\left(X - Y - \frac{1}{2}\frac{\alpha}{\alpha^2 + \beta^2}\right)\right.$$

$$+ \frac{0.129801n_e}{2\alpha} - \frac{0.010333n_e}{2\alpha}(\ln 2 + 1) - \frac{0.010333n_e}{2}\frac{\alpha}{\alpha^2 + \beta^2}$$

$$\left. + \frac{0.010333n_e}{\beta}\sum_{k=2}^{\infty}\frac{(k-2)!}{2^k} I_k\left(\frac{k\alpha}{\beta}\right) + \frac{0.010333n_e \ln n_e}{2\alpha}\right]$$

The energy of inhomogeneity can also be evaluated as an infinite series, but the terms are more complicated in form than those encountered above. We have used an extrapolation procedure to estimate the sum from the first two terms.

The electrostatic energy per unit area for a neutral system (no external field) is given by

$$E_{es} = -\pi \int_{-\infty}^{\infty} \mathrm{d}z \int_{-\infty}^{\infty} \mathrm{d}z'[n(z) - \rho(z)][n(z') - \rho(z')]|z - z'|$$

The electron-ion pseudopotential term, to be added to the electrostatic energy, is calculated as:

$$\int_{-L}^{L} \mathrm{d}z_1 \rho^{(1)}(z_1) \int \mathrm{d}\mathbf{r}_2 n(z_2)\theta(R_c - r_{12})(r_{12})^{-1}$$

$$- \int_{-L}^{Y} \mathrm{d}z_1 \left(\frac{n_e}{q}\right) \int \mathrm{d}\mathbf{r}_2 n_e \theta(R_c - r_{12})(r_{12})^{-1} = 2\pi\left[\int_{-\infty}^{\infty} \mathrm{d}z_1 \rho^{(1)}(z_1)\right.$$

$$\left. \times \int_{z_1 - R_c}^{z_1 + R_c} \mathrm{d}z_2 n(z_2)(R_c - |z_{12}|)\left(\frac{n_e^2}{q}\right) - \int_{-\infty}^{Y} \mathrm{d}z_1 \int_{z_1 - R_c}^{z_1 + R_c} \mathrm{d}z_2 (R_c - |z_{12}|)\right]$$

and leads to a rather complicated algebraic expression. The exclusion part of the ion-ion term, to be subtracted from the electrostatic energy, may be obtained from the pseudo-potential term by replacing $n$ by $\rho^{(1)}$ and $R_c$ by $d$, and multiplying by $\frac{1}{2}$.

We have performed calculations for the two systems Cs and Li for $\beta \neq 0$ and compared with results for $\beta = 0$. Several values of $\lambda$ were considered for each. In every case, we have found the minimum in $U^s$ with respect to $\alpha$ and $\beta$ simultaneously. For Cs, the use of $\beta$ gives a negligible change, even though the best $\alpha$ for $\beta = 0$ differs appreciably for the best $\alpha$ when $\beta \neq 0$. In the case of Li, the changes on allowing $\beta$ to vary are still quite small in relative terms (tenths of a per cent), but noticeable in absolute terms (21 dyne/cm for $\lambda = 1$). The actual values of $\beta$ are quite different from those appropriate to Friedel oscillations.