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Density-functional theory of the surface tension of simple liquid metals

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A general density-functional formalism for an inhomogeneous liquid metal is described. The free energy is expressed in terms of two densities: electronic and ionic. In the limit of small spatial density variations of arbitrary wave number, the electron density can be eliminated exactly and the free energy expressed as a functional of the ionic density alone, although the electronic degrees of freedom are still implicitly present. This formalism is applied within the gradient approximation to calculate the surface tension and surface widths of a number of simple liquid metals. The free-energy density is evaluated within the structural expansion in conjunction with a hard-sphere variational approximation to treat the liquid structure, and the gradient coefficient is calculated using a mean-spherical-like approximation to estimate the direct correlation function. This first-principles calculation thus has as input only a parameter describing the pseudopotential and the bulk liquid density. Results for the surface tension of the alkali metals are in excellent agreement with experiment. The temperature derivative of the surface tension is calculated to within a factor of 3 of experiment and probably within experimental error bars. Results for Al and Zn lead to a surface tension which is considerably larger than experiment. Surface widths are in all instances computed to be quite narrow but in reasonable agreement with available experiment. It is argued that discrepancies for the polyvalent metals arise not from the theory itself but rather from difficulty in calculating parameters of the theory from first principles. To verify this, a simple scaling form for surface tension is proposed, motivated by the density-functional theory but in which the relevant parameters are estimated in terms of the liquid density and melting temperature. Agreement with experiment for the scaling expression is at least as good as existing empirical expressions. Finally, a formalism is described which permits, in principle, calculation of both the electronic and ionic singlet density near the liquid surface. Both one-body and two-body forces are obtained, although no numerical evaluations of these are presented. The possible relevance of these to liquid surface structure is briefly discussed.

I. INTRODUCTION

The surface properties of liquid metals are of interest for a number of reasons, both fundamental and technological. Since they are simple liquids (in the sense of having a structure dominated by two-body central forces), liquid metals might be predicted to behave in their surface properties very much like simple nonmetallic liquids, such as liquid Ar. On the other hand, because they are metals, their surface tensions might be expected to be very similar to the surface energies of solid metals; this is often assumed in solid-state calculations, in which zero-temperature surface energies are compared to extrapolated liquid-state surface tensions. Because electrons in solid metals are known to be strongly perturbed by surfaces, the same might be anticipated in liquid metals. Thus the conventional linear-response theory which is used to treat electrons in bulk free-electron liquid metals[1] might be predicted to work poorly at liquid-metal surfaces. Even worse, from the point of view of any perturbation theory that might be applied, a liquid-metal surface is actually the boundary between a metallic liquid and a nonmetallic vapor, and a good theory of the surface must at least consider the possibility of a metal-nonmetal transition at the surface.

From a practical point of view, surface-tension forces are of importance in many applications involving liquid metals. In the low-gravity environment of space, for example, where gravity-driven convection is minimized, so-called Marangoni convection, due to surface-tension gradients, becomes important. The driving force for this process is the derivative of the surface tension with respect to any physical quantity (temperature, concentration) which may be varying parallel to the surface. Because such derivatives are very difficult to measure accurately, any theory which can shed light on these gradients, either for specific metals or for liquid metals generally, may be useful.

In the past few years a number of theorists have developed new approaches to liquid-metal surfaces, among them Evans and collaborators,[2] Hasegawa and Watabe,[3] D'Evelyn and Rice,[4] and Mon and Stroud.[5] Most of these have tended to be generalizations of the original work of Lang and Kohn[6] on solid metal surfaces, but suitably modified to apply to liquids, and they have achieved varying degrees of success when applied to liquid surfaces.

The present paper is an attempt to approach the problem from a slightly different point of view—namely, by generalizing a simple theory of classical fluids which has proven successful when applied to Ar and similar materials. The method to be used is a variant of a classical density-functional formalism introduced by Ebner, Saam, and Stroud[7] in 1976. This method was previously used, in a very simple phenomenological form, by Mon and Stroud[5] to calculate with success both the surface tension and surface widths of a number of simple liquid metals. The present work takes a similar approach but calculates all the input parameters (except for the bulk liquid density) from first principles instead of fitting them to experiments, as was done by Mon and Stroud. Our results for the surface tensions of the alkali metals prove to be within a few percent of experiment. Agreement for the polyvalent metals studied (Al and Zn) is not good, for reasons to be discussed below. The surface widths in all cases are found to be quite narrow, in agreement with previous calculations by other workers by quite different techniques, but in disagreement with Mon and Stroud. In the case for which a temperature derivative was calculated (Na) agreement with experiment is reasonable, although the error bars for experiment are so substantial as to make quantitative comparison impossible.

We turn now to the body of the paper. Section II gives a derivation of the necessary formalism. In particular, it shows how a two-component inhomogeneous electron-ion fluid (i.e., an inhomogeneous liquid metal) can be systematically reduced to a one-component inhomogeneous fluid. This derivation provides the proof that, in the weak pseudopotential approximation, the electronic degrees of freedom can be integrated out and the inhomogeneous liquid metal reduced to an inhomogeneous one-component fluid with effective interactions. Section III presents the application of the formalism to a number of liquid metals and gives some empirical rules for estimating surface tensions and derivatives of surface tensions, as deduced from these results. At the end of Sec. III contact is made with the better known solid-metal surface electronic density-functional calculations and the differences in approach are discussed. A more complex formalism is outlined in Sec. IV, in a form which treats the electronic and ionic densities as independent variables, but no numerical applications are presented here. Finally, a brief discussion follows in Sec. V.

II. FORMALISM

A. Reduction to a quasi-one-component inhomogeneous fluid

A liquid metal with a surface is intrinsically inhomogeneous: The electronic and ionic number densities $n_e(\vec{x})$ and $n_i(\vec{x})$ vary in a (presumably) continuous way from the high-density liquid metallic side to the low-density nonmetallic vapor. Thus in order to understand the thermodynamics of the liquid-metal surface one requires a model for the free energy of an inhomogeneous liquid metal. Such a model is made possible by a theorem of Hohenberg and Kohn.[8] For present purposes, the theorem states that the Helmholtz free energy F of an inhomogeneous liquid metal is a unique functional of the electronic and ionic number densities

$$F=F[n_e(\vec{x}),n_i(\vec{x}),T]\ . \tag{2.1}$$

The theorem also states that the system chooses densities $n_i(\vec{x})$ and $n_e(\vec{x})$ so as to minimize the functional F, consistent with any given boundary conditions. Here $n_i(\vec{x})$ and $n_e(\vec{x})$ are the ensemble-averaged number densities and for our purposes the appropriate ensemble will usually be one of fixed T and pressure P, suitable for describing a liquid phase in equilibrium with its vapor.

The form of the functional F is not known in general. However, for weakly inhomogeneous systems in which n_i and n_e vary by only small amounts (but with arbitrary wave vector), it may be expanded in a Taylor series

$$F=F_0[\bar{n}_e,\bar{n}_i,T] +\frac{1}{2}\sum_{\alpha=1}^{2}\sum_{\beta=1}^{2}\int\int d\vec{x}\,d\vec{x}'G_{\alpha\beta}(\vec{x}-\vec{x}')\delta n_\alpha(\vec{x})\delta n_\beta(\vec{x}')\ , \tag{2.2}$$

where $\delta n_\alpha=n_\alpha(\vec{x})-\bar{n}_\alpha$, and α,β are indices which run over the two constituents (electrons and ions), the kernels $G_{\alpha\beta}$ depend only on the difference $\vec{x}-\vec{x}'$ because of the homogeneity of the reference system, and they also depend implicitly on $\bar{n}_e$, $\bar{n}_i$, and T.

Following Hohenberg and Kohn[8] and Ebner, Saam, and Stroud,[7] we can relate the kernels $G_{\alpha\beta}$ to the density response functions for a *uniform* reference system by imagining the two-component liquid metal to be subjected to a fictitious external potential. This potential adds to the free energy (2.2) a term of the form

$$H'=\sum_{\alpha=1}^{2}\int d\vec{x}\,\delta n_\alpha(\vec{x})V_\alpha^{\text{ext}}(\vec{x})\ . \tag{2.3}$$

The true density profile is then obtained by minimizing the sum of (2.2) and (2.3) with respect to $\delta n_\alpha(\vec{x})$. The result is

$$\delta n_\alpha(\vec{q})=-\sum_{\beta=1}^{2}\{[\overleftrightarrow{G}(\vec{q})]^{-1}\}_{\alpha\beta}V_\beta^{\text{ext}}(-q)\ . \tag{2.4}$$

Here the various quantities in (2.4) are Fourier transforms defined by

$$\begin{aligned}\delta n_\alpha(\vec{q})&=\int d\vec{x}\,\delta n_\alpha(\vec{x})e^{i\vec{q}\cdot\vec{x}}\ ,\\ V_\alpha(\vec{q})&=\int d\vec{x}\,V_\alpha(\vec{x})e^{i\vec{q}\cdot\vec{x}}\ ,\\ G_{\alpha\beta}(\vec{q})&=\int d\vec{x}\,G_{\alpha\beta}(\vec{x})e^{i\vec{q}\cdot\vec{x}}\ ,\end{aligned} \tag{2.5}$$

and $\overleftrightarrow{G}^{-1}$ denotes the matrix inverse of $\overleftrightarrow{G}(\vec{q})$. Comparing (2.4) with the usual definition[9] of density-density response functions or susceptibilities, we see that

$$G_{\alpha\beta}(\vec{x})=-\frac{1}{(2\pi)^3}\int d\vec{q}\,e^{-i\vec{q}\cdot\vec{x}}\{[\overleftrightarrow{\chi}(\vec{q})]^{-1}\}_{\alpha\beta}\ , \tag{2.6}$$

where $\overleftrightarrow{\chi}(\vec{q})$ is the 2×2 susceptibility matrix of the coupled electron-ion system.

Although (2.2) and (2.6) are exact as they stand (in the limit of small δn_i and δn_e), they are of limited utility because of the difficulty in calculating the three partial susceptibilities involved in the inhomogeneous terms. The form of the functional simplifies considerably, however, if we carry out the variational minimization to solve for δn_e in terms of δn_i (physically motivated by the adiabatic approximation) thereby expressing the free energy in terms of the ionic density alone. We rewrite (2.2) as

$$F=F_0+\frac{1}{2\Omega}\sum_{\vec{q}\neq 0}\{G_{ee}(q)\,|\,\delta n_e(q)\,|^2 + [G_{ei}(q)\delta n_e(q)\delta n_i^*(q)+\text{c.c.}] + G_{ii}(q)\,|\,\delta n_i(q)\,|^2\}\;, \qquad (2.7)$$

where Ω is the volume of the system. Minimizing (2.7) with respect to $\delta n_i(q)$ gives an expression for δn_e

$$\delta n_e(q)=-\frac{G_{ii}(q)}{G_{ei}(q)}\delta n_i(q) \qquad (2.8)$$

with an equivalent expression for $\delta n_e^*(q)$. Substitution of (2.8) back into (2.7) gives (using the fact that the various coefficients G are all real)

$$F=F_0+\frac{1}{2\Omega}\sum_{\vec{q}\neq 0} G_{\text{eff}}(q)\,|\,\delta n_i(q)\,|^2\;, \qquad (2.9)$$
$$G_{\text{eff}}=G_{ii}-\frac{G_{ie}^2}{G_{ee}}=-[\chi_{ii}(q)]^{-1}\;,$$

where we have used the relation (2.6) to connect the matrix elements of $\overleftrightarrow{G}$ to those of $\overleftrightarrow{\chi}$.

The result (2.9) has a very simple and appealing interpretation. It states that, at least for weakly inhomogeneous two-component fluids such as liquid metals, the second component (the electrons) can be eliminated in favor of the first (the ions) and the free energy can be expressed *exactly* as a functional of the ionic density *alone.* This is the analog for inhomogeneous liquid metals of the usual method of treating homogeneous metals, whereby the electronic degrees of freedom are systematically eliminated from the description of the fluid.[10] Note that the electrons are still *implicitly* present in the functional (2.9) in two places: the uniform free energy F_0 and the response function $\chi_{ii}(q)$. F_0 has, as is well known, a large electron-gas contribution. For a classical ionic fluid, $\chi_{ii}(q)$ is related to the ionic structure factor $S(q)$ by[1]

$$\chi_{ii}(q)=-\frac{\bar{n}_i}{k_B T}S(q)\;, \qquad (2.10)$$

where $\bar{n}_i$ is the ionic density as before. It can also be related to the so-called direct correlation function $C(r)$, defined by[1]

$$[1-\bar{n}_i C(q)]^{-1}=S(q)\;. \qquad (2.11)$$

The structure factor, although it describes correlations between ionic positions, is still very sensitive to the electrons. These electrons screen the ions and thereby help to determine the ion-ion forces which, in turn, control $\chi_{ii}(q)$. Note also that the result (2.9) does not depend on any particular categorization of electrons as belonging to the "conduction" or "core" group. It is thus valid in both the metallic liquid and the nonmetallic vapor on either side of the interface.

B. Alternate forms of the density-functional gradient expansion

The result (2.9) can be rewritten in a form which makes it more readily extended to liquids which are *very* nonuniform. We first rearrange the terms in (2.9) as

$$F=\int f(\bar{n})d\vec{x} -\tfrac{1}{4}\int d\vec{x}\,d\vec{x}'G_{\text{eff}}(\vec{x}-\vec{x}')[\delta n(\vec{x})-\delta n(\vec{x}')]^2 +\tfrac{1}{2}\int d\vec{x}\,d\vec{x}'G_{\text{eff}}(\vec{x}-\vec{x}')[\delta n(\vec{x})]^2\;, \qquad (2.12)$$

where $f(\bar{n})$ is the Helmholtz free energy of the liquid per unit volume at density $\bar{n}$, $\delta n(\vec{x})=n(\vec{x})-\bar{n}$, and we have suppressed the subscript denoting ionic density. The first integral in (2.12), of course, is simply the uniform free energy F_0 written out in terms of a free-energy density. Next using the relationship[11]

$$G_{\text{eff}}(r)=-k_B T C(r)\;, \qquad (2.13)$$

where $C(r)$ is the direct correlation function whose Fourier transform is defined in Eq. (2.11), and the compressibility sum rule

$$S(q=0)=[1-\bar{n}C(0)]^{-1} =\bar{n}k_B T K_T=\frac{k_B T}{\bar{n}(\partial^2 f/\partial n^2)_{T,\bar{n}}}\;, \qquad (2.14)$$

where K_T is the isothermal compressibility, we can rewrite (2.12) in the form

$$F=\int\left[f(\bar{n})+\frac{1}{2}\left[\frac{\partial^2 f}{\partial n^2}\right]_{T,\bar{n}}[n(\vec{x})-\bar{n}]^2\right]d\vec{x} +\tfrac{1}{4}k_B T\int d\vec{x}\,d\vec{x}'C(\vec{x}-\vec{x}';\bar{n})[n(\vec{x})-n(\vec{x}')]^2\;. \qquad (2.15)$$

Finally, we observe that the quantity in large square brackets represents the first two terms in a Taylor series for $f(n(\vec{x}))$, the free energy per unit volume of a liquid of ionic density $n(\vec{x})$. Thus to this order we obtain the result of Ebner *et al.* for a *one*-component fluid:

$$F[n(\vec{x})]=\int f(n(\vec{x}))d\vec{x} +\tfrac{1}{4}k_B T\int d\vec{x}\,d\vec{x}'C(\vec{x}-\vec{x}';\bar{n}) \times[n(\vec{x})-n(\vec{x}')]^2\;, \qquad (2.16)$$

which was previously used by a number of workers to treat *insulating* fluids and is here shown to be correct also for *metallic* fluids, through second order in the density fluctuations $n(\vec{x})-\bar{n}$.

Although (2.16) is not exact beyond second order in the density fluctuations $\delta n(\vec{x})$, it is reasonable to assume that this *form* may still be approximately valid when the fluctuations are larger, as at a surface. In that case the kernel $K(\vec{r}-\vec{r}\,';\bar{n})$ in the interaction term [the second integral in (2.16)] must be evaluated at some suitable intermediate value of density $\bar{n}$. Calculations carried out in Ref. 7 indicate that for any reasonable choice of $\bar{n}$ the surface tension and width remain little modified, at least for insulating fluids.

If the density $n(\vec{x})$ is sufficiently slowly varying, the nonlocal second term in (2.16) can be expanded in a Taylor series and the result expressed in terms of the density gradient:

$$F[n(\vec{x})]=\int f(n(\vec{x}))d\vec{x}+\int K(\bar{n}(\vec{x}))\,|\vec{\nabla}n\,|^2 d\vec{x}\ , \tag{2.17a}$$

$$K(\bar{n})=\frac{k_BT}{12}\int C(r;\bar{n})r^2 d\vec{x}\ . \tag{2.17b}$$

This is the form which has been used in the calculations to be presented below. It is exact to second order in the density fluctuations, in the limit of an ionic density which is slowly varying in space on a scale set by the variations in $C(r;n)$. We shall present numerical evidence below that the gradient expansion whose first terms are represented by (2.17) does indeed converge for most liquid metals: This stands in contrast to the analogous expansion for a quantum fluid such as an electron gas at $T=0$, for which the convergence is dubious; see the discussion at the end of Sec. III.

C. Relation to surface tension

Given a method for calculating the free energy of an inhomogeneous fluid, it is a short step to write an expression for the surface tension of the liquid in equilibrium with its vapor. For a liquid in equilibrium with its vapor at pressure P, temperature T, the relevant thermodynamic potential to be minimized is the "grand free energy"

$$\Omega[n(\vec{x})]=F[n(\vec{x})]-\mu\int n(\vec{x})d\vec{x}\ , \tag{2.18}$$

where μ is the chemical potential for the ions. The surface tension is the extra grand free energy per unit area due to the presence of the surface. If we use form (2.17) for the Helmholtz free-energy functional and assume a planar surface, the integral form for the surface tension is

$$\tau=\int_{-\infty}^{\infty}[f(n(z))-\mu n(z)+P]dz + \int_{-\infty}^{\infty}K(\bar{n}(z))\left[\frac{dn}{dz}\right]^2 dz\ , \tag{2.19}$$

while if the full nonlocal functional (2.16) is used the last term in (2.19) is replaced by the term

$$\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dz'H(z-z';\bar{n})[n(z)-n(z')]^2\ , \tag{2.20a}$$

$$H(z;\bar{n})=\frac{\pi}{2}k_BT\int_0^{\infty}\rho\,d\rho\,C[(\rho^2+z^2)^{1/2}]\ , \tag{2.20b}$$

and $\bar{n}$ is some suitable intermediate density. Expression (2.20) results from partially integrating the nonlocal term in (2.16) for a planar surface, assuming n depends only on the z coordinate and that $C(\vec{r}-\vec{r}\,')$ depends only on the difference $|\vec{r}-\vec{r}\,'|$, as will be the case for an isotropic fluid. In the present work, the gradient form [Eq. (2.19)] has been used for all calculations. As may be seen it defines a *variational principle* for the surface tension: τ is the minimum value of the right-hand side of (2.19) over all possible values of the function $n(z)$ consistent with the boundary conditions. The boundary conditions for a planar surface are, of course (taking the vapor phase to fill the half-space $z<0$),

$$\begin{aligned} &n\rightarrow n_l\quad (z\rightarrow+\infty)\ ,\\ &n\rightarrow n_v\quad (z\rightarrow-\infty)\ , \end{aligned} \tag{2.21}$$

where n_l,n_v represent the equilibrium densities of the uniform liquid and vapor phases at temperature T, pressure P. The corresponding function $n(z)$ which minimizes (2.19) represents the equilibrium surface profile within this formalism. In general, the minimization of (2.19) must be done numerically, although for special forms of the function $f-\mu n+P$ an analytic solution is available.[5] The minimization condition can be written as a Schrödinger-type differential equation, but in practice this form is probably not of greater utility than the original integral form.

Two further points about (2.19) are in order. The pressure P is present in the equation, of course, because the asymptotic form of the grand potential far from the surface in both the liquid and vapor phases is $-P$, which must be subtracted to give the *extra* free energy due to the surface. Also, in this as in other previous formulas, we have suppressed the temperature dependence of the functions f and K.

III. RESULTS

We next apply the preceding formalism to the surfaces of several simple (i.e., nearly-free-electron) liquid metals. We first describe microscopic calculations within the gradient formalism, and then analyze the results from the point of view of a simple scaling argument which leads to an empirical relationship between the surface properties of liquid metals and various bulk parameters.

A. Microscopic calculations

The gradient expression for the surface tension [Eq. (2.19)] relates τ to two density-dependent bulk properties of a *uniform* metallic fluid: the free-energy density $f(n,T)$ and the direct correlation function $C(r;n,T)$. Both of these, in principle, must be computed as a function of density, at densities ranging between those of the uniform liquid metal and that of the uniform vapor in equilibrium. Since this is a density range over which a metal-nonmetal transition occurs, it will naturally be very difficult to construct a theory for f and C which treats *both* limiting densities correctly. We have therefore sidestepped this problem by using an approach which is appropriate in the *metallic* limit. The justification for this is basically intuitive: One expects the surface properties of the liquid to be dominated by the metallic regime, since the vapor (at temperatures near the triple point) is of very low density. For this reason, for all of the numerical calculations below we have taken the vapor density n_v to be zero.

For the free-energy density $f(n,T)$ we use the structural expansion as described, for example, by Ashcroft and Stroud.[1] Within this approach the Helmholtz free energy per *ion*, $F(n,T)=f(n,T)/n$, is given as

$$F=E_{\text{Mad}}+E_{eg}+E_{\text{BS}}^{(2)}+E_0+\tfrac{3}{2}k_BT -T(S_{\text{ion}}^{\text{ideal}}+S_{\text{ion}}^{\text{ex}}+S_{\text{ele}}) \,. \tag{3.1}$$

Here E_{Mad} is the Madelung energy, E_{eg} the kinetic, exchange, and correlation energy of the conduction-electron gas, $E_{\text{BS}}^{(2)}$ the so-called band-structure energy evaluated to second order in the electron-ion pseudopotential, E_0 the Hartree energy, $\frac{3}{2}k_BT$ the kinetic energy per ion, $S_{\text{ion}}^{\text{ideal}}$ the ideal-gas contribution to the ionic entropy, $S_{\text{ion}}^{\text{ex}}$ the excess ionic entropy, and S_{ele} the electronic entropy. The Madelung term in Eq. (3.1) may be evaluated analytically if the liquid structure factor is taken to be that of a hard-sphere fluid, as given by the Percus-Yevick approximation. The resulting expression for E_{Mad} is (in hartrees per ion)

$$E_{\text{Mad}}=-\frac{3Z^{5/3}}{r_s/a_0}\,\frac{1-\eta/5+\eta^2/10}{1+2\eta}\,, \tag{3.2}$$

where η is the hard-sphere packing fraction, equal to the volume fraction of the fluid occupied by the hard-sphere reference system, Z is the valence, r_s is the usual electron density parameter defined by $n_e=(4\pi/3r_s^3)^{-1}$, and a_0 is the Bohr radius. Similarly,

$$E_{eg}=Z\left[\tfrac{3}{10}(k_Fa_0)^2-\frac{3}{4\pi}(k_Fa_0) +\frac{1}{2}\left[-0.115+0.031\ln\frac{r_s}{a_0}\right]\right], \tag{3.3}$$

$$E_{\text{BS}}^{(2)}=\frac{2}{\pi}(k_Fa_0)\int_0^\infty dx\,\cos^2(2k_Fr_cx) \times\left[\frac{1}{\epsilon(2k_Fx)}-1\right]S_{\text{PYHS}}(2k_F\sigma x)\,, \tag{3.4}$$

$$E_0=2\pi Z^2n_{\text{ion}}a_0^3\left[\frac{r_c^{E_0}}{a_0}\right]^2, \tag{3.5}$$

and

$$S_{\text{ion}}^{\text{ideal}}=\tfrac{3}{2}\ln\left[\frac{k_BT}{(e^2/a_0)}\,\frac{1}{2\pi}\,\frac{M}{m}\right]-\ln(n_{\text{ion}}a_0^3)+\tfrac{5}{2}\,, \tag{3.6}$$

$$S_{\text{ion}}^{\text{ex}}=\frac{3}{2}\left[1-\frac{1}{(1-\eta)^2}\right]+\ln(1-\eta)\,, \tag{3.7}$$

$$TS_{\text{ele}}=\frac{1}{2}\left[\frac{\pi}{(k_Fa_0)}\,\frac{k_BT}{(e^2/a_0)}\right]^2. \tag{3.8}$$

In the above formulas, k_F is the Fermi wave vector of the conduction-electron gas [given by $k_F=(3\pi^2n_{\text{ion}}Z)^{1/3}$], M/m is the ratio of the ionic to electronic masses, r_c is the empty-core radius defining the electron-ion pseudopotential, $\epsilon(2k_Fx)$ is the dielectric function of the interacting electron gas[12] $(x=k/2k_F)$, and $S_{\text{PYHS}}(k)$ is the Percus-Yevick hard-sphere structure factor at wave vector k. The band-structure energy and E_0 are computed assuming an Ashcroft empty-core pseudopotential

$$V_p(k)=-\frac{4\pi Ze^2}{k^2}\cos(kr_c)\,, \tag{3.9}$$

where r_c is the empty-core radius. Since E_0 depends on the behavior of the pseudopotential at small values (it is the $k\rightarrow 0$ limit of the difference between the pseudo-Coulomb and bare Coulomb potential), while E_{BS} is dominated by wave vectors near the first peak of the structure factor, the same value of r_c may not be appropriate for evaluating these two terms. We have used, in fact, different values, as indicated by the superscript on the value employed in E_0. The ionic excess entropy $S_{\text{ion}}^{\text{ex}}$ is evaluated for a fluid of hard spheres of packing fraction η, as calculated from the so-called compressibility equation of state.[1]

In the present calculations the core radius r_c appearing in the band-structure energy was obtained from fits to Fermi-surface or liquid-state transport data. The Hartree core radius $r_c^{E_0}$ was regarded as a constant to be fixed by requiring that the total free energy have a minimum in the liquid metallic state at the observed melting density.[13] Table I indicates that the values obtained in this way for a variety of simple liquid metals differ by less than 15% from the values of r_c used in E_{BS}.

The free energy (3.1), evaluated with hard-sphere distribution functions, is actually an upper bound to the true free energy of the liquid metal.[1] We have determined η variationally, at each value of n_{ion} and T, by minimizing F with respect to it. For six values of $n_{\text{ion}}/n_{\text{liq}}$ $(=1.0, 0.8, 0.5, 0.2, 0.1$, and $0.01)$, η was determined in this way (n_{liq} being the density of bulk liquid) and Lagrange interpolation was then used to calculate η (n_{ion}) for a continuous range $0\le n_{\text{ion}}/n_{\text{bulk}}\le 1$.

The other quantity required for the surface tension is the gradient term in (2.19), which presupposes knowledge of the direct correlation function $C(r)$. Following Mon and Stroud, we have used the approximation

$$C(r;\bar{n})=\begin{cases}C_{\text{PYHS}}(r;\bar{n}), & r<\sigma\\ -\beta V_{ii}(r;\bar{n}), & r>\sigma\,,\end{cases} \tag{3.10}$$

where $\beta=(k_BT)^{-1}$, $C_{\text{PYHS}}(r;\bar{n})$ is the Percus-Yevick hard-sphere direct correlation function at ionic density $\bar{n}$, and $V_{ii}(r;\bar{n})$ is the effective (i.e., screened) ion-ion interaction. For the present choice of the pseudopotential[12] $V_{ii}(r;\bar{n})$ is just the Fourier transform of

TABLE I. Input parameters and thermodynamic predictions of structural expansion [Eq. (3.1)]; predicted compressibilities are via direct differentiation of free energy. The columns represent the absolute temperature T in kelvin, the liquid density n_l, the empty-core radius r_c, the value $r_c^{E_0}$ used to fit the zero-pressure density, the bulk free energy density per ion F_{bulk}, the variational packing fraction η, the experimental zero-temperature internal energy E, the calculated isothermal compressibility K_T^{th}, and the measured compressibility K_T^{expt}.

Element	T (K)	$10^3 n_l a_0^3$	r_c/a_0	$r_c^{E_0}/r_c$	$F_{\text{bulk}}/(e^2/a_0)$	η	$E_{\text{expt}}/(e^2/a_0)$	$K_T^{\text{th}}(10^{-12}\ \text{cm}^2/\text{dyn})$	K_T^{expt}
Na	371	3.598	1.69	1.083	−0.2382	0.433	−0.230	20.5	18.6
	393	3.55		1.084	−0.2385	0.424		21.3	
K	337	1.890	2.226	1.121	−0.1987	0.435	−0.195	48.6	38.2
Rb	312	1.528	2.4	1.142	−0.1878	0.435	−0.185	64.1	49.3
Cs	302	1.233	2.62	1.154	−0.1770	0.436	−0.173	82.8	68.8
Zn	693	8.994	1.27	1.015	−0.9782	0.554	−1.05	2.62	2.50
Al	914	7.872	1.12	1.092	−2.118	0.465	−2.07	2.40	2.42

$$V_{ii}(q;\bar{n})=\frac{4\pi Z^2e^2}{q^2}\left[1+\left[\frac{1}{\epsilon(q;\bar{n})}-1\right]\cos^2(qr_c)\right], \tag{3.11}$$

σ is the hard-sphere diameter appropriate to density $\bar{n}$, and we have determined this by the simple prescription

$$V_{ii}(\sigma)=\tfrac{3}{2}k_BT\ , \tag{3.12}$$

where σ is now the distance of closest approach of two interacting ions, inasmuch as σ is then the classical turning point for a thermal kinetic energy $\frac{3}{2}k_BT$. The scheme embodied in (3.10) thus accounts, albeit roughly, for both short-range hard-core and long-range correlations.

The evaluation of the integral (2.17b) required for the gradient coefficient is somewhat delicate. The reason is that in the presence of the metallic screening $V_{ii}(r)$ will exhibit Friedel oscillations[3] and decay only as $1/r^3$. Since the ion-ion pair potential is available analytically in k space, however, the contribution of the tail to the gradient coefficient is readily expressed as

$$K'_{\text{tail}}(n)=-\frac{1}{6\pi}\int_0^\infty q^2dqV_{ii}(q)\times\left[\lim_{\mu\to 0}\int_\sigma^\infty dr\, r^4\frac{\sin(qr)e^{-\mu r}}{qr}\right]. \tag{3.13}$$

The r-space integral is easily done, the limit $\mu\to 0$ is well behaved, and the tail contribution to K' is readily found by this procedure. The core contribution from $r<\sigma$ is easily obtained in closed analytic form using the Percus-Yevick hard-sphere direct correlation function. The only remaining input is the ionic chemical potential μ. This is simply the free energy per ion deep in the bulk of the liquid since the pressure $P\cong 0$ by comparison with F.

The surface tension is now obtained from the functional (2.19) as

$$\tau=\int_{-\infty}^{\infty}dz\,\Omega(n(z))+K'(n_{\text{av}})\int_{-\infty}^{\infty}dz\left[\frac{dn}{dz}\right]^2, \tag{3.14}$$

where we have made the further approximation of neglecting the density dependence of K' and replacing it by its value at the average ionic density $n_{\text{av}}=\frac{1}{2}(n_l+n_v)$, n_l and n_v being the equilibrium liquid and vapor densities. This is the density at which dn/dz is expected to be largest and where, therefore, the gradient term should be of most importance.[14] We have used a single-parameter variational trial density of the form

$$n_{\text{ion}}(z)=\tfrac{1}{2}(n_l+n_v)+\tfrac{1}{2}(n_l-n_v)\tanh(\Gamma z)\ . \tag{3.15}$$

When this form is substituted into (3.14) and the surface tension minimized with respect to Γ, the result is

$$\tau=2\sqrt{AB}\ ,\quad \Gamma=\sqrt{A/B}\ ,\quad 2w=2/\Gamma\ , \tag{3.16}$$

TABLE II. Predicted surface properties from gradient approximation for free energy [Eq. (3.16)]. The columns represent the absolute temperature T in kelvin, the variational hard-sphere diameter σ in units of the empty-core radius r_c, the gradient coefficient K', the theoretical surface tension τ_{th}, the experimental surface tension τ_{expt}, the surface halfwidth w, and the calculated derivative $d\tau/dT$.

Element	T (K)	σ/r_c	K' ($e^2-a_0^4$)	τ_{th} (dyn/cm)	τ_{expt}	w/a_0	$d\tau/dT$ (dyn/cm °C)
Na	371	3.437	29.18	213	191	1.84	$-0.28(\simeq-0.10$ expt)
	393	3.428	29.08	207		1.83	
K	337	3.18	68.59	112.2	115	2.27	
Rb	312	3.12	88.0	89.0	85	2.40	
Cs	302	3.06	117.2	71.9	70	2.58	
Zn	693	3.97	47.9	1936	782	2.08	
Al	914	4.29	79.9	2709	914	1.90	

with

$$A=\int_{-\infty}^{\infty} d(\Gamma z)\Omega(n(z)) \, , \qquad B=\frac{K'(n_{\text{av}})}{3}(n_l-n_v)^2 \, , \tag{3.17}$$

which explicitly gives both the surface tension and surface width in terms of properties of a homogeneous liquid metal; here $2w$ is a reasonable estimate of the 10—90% interface width (see below). Of course, in contrast to the Ginzburg-Landau calculations of Mon and Stroud, the choice (3.15) does not give an *exact* minimization of the surface-tension functional. As mentioned above, we have taken $n_v=0$.

The results of our calculations are summarized in Tables I and II. We have examined all the alkali metals except Li, a metal for which a local pseudopotential of the empty-core genus is very probably inadequate, and we have also carried out full calculations for two representative polyvalent metals: Zn and Al. It is evident that agreement between the experimental and calculated surface tensions of the alkalis is remarkably good—better than that obtained by Mon and Stroud—and it must be emphasized that these numbers are obtained with *no adjustable parameters whatsoever,* but are entirely first principles, except for the use of a simple model pseudopotential to represent the electron-ion interaction and the use of the experimental bulk liquid density. In contrast, the results for the polyvalent metals are less satisfactory, the calculated surface tension being a factor of 2.5 too large in the case of Zn and a factor of 3 for Al. The calculated surface *widths* $2w$ in all cases are quite narrow,[15] generally about 2 Å. Although experimental data are sparse, available evidence for Cs (Ref. 15) and Hg (Ref. 16) suggests that our model may be leading to a surface width which is too narrow.

We have also made an estimate of the temperature derivative $d\tau/dT$ of the surface tension for one liquid metal, namely, Na, for which our calculation of the surface tension itself is in good accord with experiment. As may be seen from Table I, the theoretical derivative is rather larger than experiment, although the experimental data itself is so uncertain that theory may be within the experimental error bars.[17,18]

In view of the excellent agreement between theory and experiment for the alkali metals and the less satisfactory results for the polyvalents, it seems worthwhile to examine the inputs to the density-functional theory in an attempt to understand just where the discrepancies originate. The main problem is most likely *not* the density-functional theory itself, which is *exact* in the limit of small density fluctuations, but rather in its execution. The implementation above made use of a number of approximations, namely: (i) the replacement of the full nonlocal theory by a local, gradient theory, (ii) extrapolation of the gradient theory to large density variations, i.e., a surface where conceivably higher powers of dn/dz might become important, and (iii) the calculation of the *inputs* to the theory, $f(n(z))$ and $C(r;n)$. Of these three, (iii) is the most likely source of inaccuracy because both f and C must be extrapolated to densities far away from the metallic densities where they can be calculated with reasonable accuracy.

Our calculations for $f(n)$ near liquid metallic densities are undoubtedly reasonable. This is shown by a comparison of experimental and theoretical compressibilities of pure liquid metals, the theoretical numbers being obtained from $K_T=[n^2(\partial^2 f/\partial n^2)_T]^{-1}$. Agreement is good, although the bulk compressibility K_T is generally overestimated by the structural expansion, as has been observed by other workers.[17] An alternative route to the compressibility sum-rule result using the Percus-Yevick hard-sphere reference system

$$K_T=\left[\frac{(1-\eta)^4}{(1+2\eta)^2}\frac{1}{na_0^3}\frac{e^2/a_0}{k_B T}\right]_{n=n_{\text{bulk}}} \tag{3.18}$$

is in generally good accord with the compressibility as obtained via the thermodynamic derivative.

The variation of $f(n)$ with n at lower density is more difficult to compare with experiment, since most of this region constitutes an "expanded" metal which cannot exist as a uniform phase in thermodynamic equilibrium. However, the surface tension is probably insensitive to the behavior of $f(n)$ at *very* low densities. To understand this we consider Fig. 1, which shows $f-\mu n$ plotted as a function of n for two representative liquid metals, Na and Al (as calculated in the structural expansion). Both show rather similar shapes having a strong peak at about $\frac{1}{5}$ the homogeneous liquid density, and tend to zero at zero density, which is the uniform vapor density to a good approximation. As is evident from Eq. (3.17), the surface tension is closely related to an integral which depends mainly on the area under this curve. It is thus not too sensitive to what happens at low densities, where $f-\mu n$ is small anyway.

It is interesting to compare $f-\mu n$ as calculated within the structural expansion to that obtained by Mon and

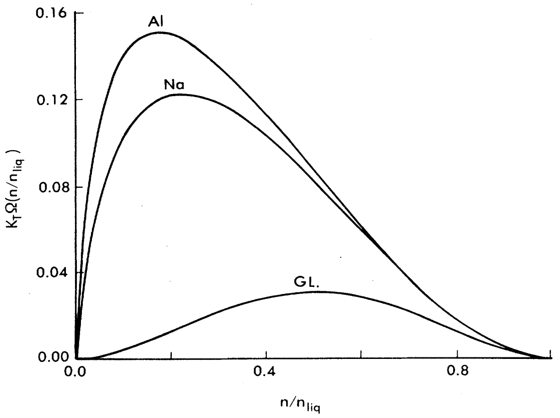

FIG. 1. Density dependence of (nongradient) free-energy—density functional: structural expansion results [Eq. (3.1)] for Na and Al, and Ginzburg-Landau form (GL) (see Ref. 5).

Stroud using a Ginzburg-Landau extrapolation procedure. As may be seen, the former leads to an area under the curve which is larger by a factor of about 5 than the latter. Both behave very similarly near the liquid density; this is because the Ginzburg-Landau theory has parameters which are guaranteed (by construction) to have the correct liquid-state compressibility, which is quite well reproduced by our structural expansion. However, the Ginzburg-Landau result deviates strongly from the structural expansion at lower densities. While our calculation is more microscopic, it is difficult to say which is more correct at lower densities. We note also that, although Na and Al are quite different in their properties as uniform liquid metals (their compressibilities differ by a factor of 8, for example), the free-energy curves, as obtained in the present work, have remarkably similar *shapes*. We exploit this similarity below in obtaining a simple scaling description of the surface properties of liquid metals.

As far as our calculation of $C(r;n)$ is concerned, substantial improvement may be possible. The approximation used here probably overestimates the strength of the gradient term in Al and Zn, most likely by exaggerating the contribution of the tail in the potential to this gradient. If a better approximation were available it might lead to more accurate surface tensions.[19] (See note added in proof.)

B. Scaling results

While the theory presented above gives a good first-principles account of the surface tension of monovalent simple liquid metals, it seems useful to generalize the underlying physics of our results to metals for which a detailed calculation is unreliable at present, e.g., the polyvalent metals. This simple generalization is based on three observations:

(i) The total area under the curve of $K_T\Omega(n/n_{\text{liq}})$ vs n/n_{liq} is roughly independent of material parameters, as is shown in Fig. 1. This is a numerical confirmation of one of the predictions of the Ginzburg-Landau theory of Mon and Stroud, which leads to an area which is a universal constant independent of material.

(ii) The effective hard-sphere packing fraction η for all liquid metals is roughly a constant (equal to 0.45) at melting $T=T_m$.

(iii) The gradient energy coefficient K', of dimensions (Hartree-Bohr[5]) must be given at melting by the relevant energy and length scales of the problem, namely, k_BT_m and the effective hard-sphere diameter σ related to η by $(\pi/6)\sigma^3 n=\eta$.

Combining (ii) and (iii) leads to the relation

$$K' \propto (k_BT_m)n_l^{-5/3} \tag{3.19}$$

and using (i) in conjunction with Eqs. (3.16) and (3.17) (and $n_v \sim 0$) gives

$$\tau = C\left[\frac{T_m}{K_T}\right]^{1/2} n_{l,\text{melting}}^{1/6} \; . \tag{3.20}$$

To test the predictions of this simple scaling form for τ (at melting) we fix the constant C by forcing (3.20) to fit the observed surface tension for Na. The predictions based on this value of C are shown in Fig. 2 and are seen to be in remarkably good agreement with experiment for a wide variety of metals.

The present scaling theory is not, of course, the first empirical formula which attempts to relate the surface tension of liquid metals to bulk properties.[18] However, it differs from previous versions because it can be derived, via definite assumptions, from a density-functional theory of the liquid-metal surface. The empirical content consists of *ad hoc* estimates of the inputs to the density-functional theory K' and the parameter A in Eq. (3.16). The estimate of K' is based on the assumption that the ion-ion pair potential [which determines $C(r)$ and hence K'] has a depth which scales as the melting temperature

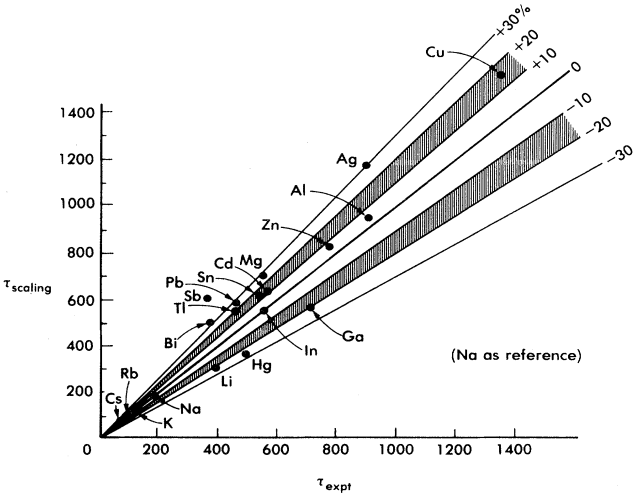

FIG. 2. Comparison with experiment of empirical density-functional scaling prediction for surface tension at melting [Eq. (3.20)].

and a range which scales as the hard-sphere diameter. This is a reasonable assumption for most liquids, nonmetallic as well as metallic. Our assumption for the free-energy density has actually been confirmed in the present work by microscopic calculations for several liquid metals, as illustrated for Na and Al in Fig. 1. It represents a kind of "law of corresponding states" for liquid metals which seems on the basis of our work to hold reasonably well for metals near melting. Thus we regard the success of the scaling estimates as evidence that the density-functional theory is adequate for liquid metals, if only good estimates of the input parameters are available.

At this point, as a prelude to Sec. IV, it may be useful to contrast our approach with the better known *electronic* density functionals in current use for calculating the *surface energies* of solid metals.[20–24] By choosing to perform a classical *ionic* density-functional calculation for the surface tension we have effectively traded the problem of finding the ground-state energy and density profile for an inhomogeneous electron gas with a surface for the problem of calculating the (finite-temperature) thermodynamics of a classical system of ions (with their adiabatically following electron screening cloud) with a surface.

While the classical approach may appear more difficult, it results in several simplifications. First, the theory above has as its central variable the thermodynamic average singlet ion density $n_i(\vec{r})$. At a bulk surface $n_i(\vec{r})$ depends only on the coordinate perpendicular to the liquid/vapor interface [neglecting capillary waves, whose effects on $n_i(\vec{r})$ should average out, and whose effects on the surface tension are expected to be small for liquid metals]. By contrast, in electron density-functional calculations for solid-metal surfaces the electron density must have the symmetry of the lattice parallel to the surface. This is a somewhat delicate matter for most electron density-functional calculations since they are frequently based on a planar uniform background calculation to which one then appends the effects of ion discreteness by low-order perturbation theory (using homogeneous[6,20–23] or inhomogeneous[24] electron-gas response functions). The second simplification follows trivially from the first: One need not select a planar uniform background model for $n_i(\vec{r})$. (The resulting electron profile can be calculated via linear response—see Refs. 10 and 27.)

In the calculations above the discrete nature of the ions might appear to have been eliminated by the thermodynamic averaging implicit in the description of a classical liquid. This is not the case: Ionic discreteness gives rise directly to the local structure of the fluid as embodied in $S(k)$ used in the local contribution to the free energy (and in our case the choice of a hard-sphere reference system) and in $C(r)$ (used in the calculation of the gradient coefficient), where both a hard-sphere and a screened discrete ion-ion interaction contribution appear.

There are several points of similarity between the electronic and ionic density-functional approaches, however. For example, on the basis of electron density-functional calculation one might reasonably object to the use of a gradient approximation above. The point to be made, however, is simply that the regimes of validity for the electronic and classical ionic gradient approximations may not be the same for electrons and ions with the same density gradient. As a crude estimate we note that, neglecting exchange-correlation effects, the gradient coefficient for electrons is[21] (in Hartree-Bohr[5])

$$K'_{\mathrm{el}} = \frac{1}{72\bar{n}_e a_0^3} , \tag{3.21}$$

while for ions [Eq. (2.17b)]

$$K'_i = (k_B T/12) \int d\vec{r}\, r^2 C(r;\bar{n}_i;\bar{n}_e) .$$

Following the arguments leading to Eqs. (3.19) and (3.20) we may take K'_i to be

$$K'_i \sim k_B T_m, \quad \sigma^5 \sim [k_B T_m/(e^2/a_0)](\bar{n}_i a_0^3)^{-5/3}$$

at melting, assuming $C(r) \lesssim 1$. Since $\bar{n}_e = Z\bar{n}_i$ for valence Z

$$\frac{K'_i}{K'_e} \sim 6 \frac{k_B T_m}{e^2/a_0} \frac{Z}{(\bar{n}_i a_0^3)^{2/3}}$$

$$\sim 0.3\text{—}0.5, \ \text{alkalis} ; \ 0.6, \ \text{Zn}; \ 1.3, \ \text{Al} . \tag{3.22}$$

Hence the question of the adequacy of the gradient approximation within a classical density-functional formalism deserves further scrutiny.[25] Since the arguments for K'_i leading to Eq. (3.19) seem to work well in the phenomenological expression (3.20), we feel that the poor results of the microscopic calculation above for the polyvalents probably are not directly attributable to a breakdown of the gradient approximation. (See note added in proof.)

IV. TWO-COMPONENT FORMALISM

In the previous sections we have discussed the surface properties of liquid metals, treating them as effectively one-component fluids—in effect, via a pseudoatom formalism in the sense discussed by Ziman.[26] This approach may be adequate for treating such quantities as the surface tension and possibly the surface width, although the results obtained in Sec. III via an approximate version of this formalism are not wholly satisfactory. One could, in fact, obtain the electron density profile $\delta n_e(z)$ by calculating the linear response of the electrons to the perturbation $Ze\delta n_{\mathrm{ion}}(z)$.[27] However, the calculation of quantities which depend sensitively on the electronic *and* ionic profiles, e.g., the electric dipole amplitude and layer thickness, may be addressed only through a formalism in which the electronic and ionic densities are both treated explicitly from the outset. In this section we outline such a formalism. Our approach bears some similarities to those of other workers, in particular Evans and collaborators, D'Evelyn and Rice, and others, but in view of various differences it seems worthwhile to present our approach as a possible, relatively simple alternative. Since numerical execution entails a substantial calculation, it will be deferred to a planned subsequent paper.

We consider an inhomogeneous liquid metal in which the ions are subjected to an external potential $W_{\text{ext}}(\vec{x})$. (The external potential is simply an artificial device to generate the inhomogeneity.) The Helmholtz free energy of the system can be written

$$F=-k_BT\ln \text{Tr}_{\text{ion}}\text{Tr}_e\exp(-H/k_BT)\ , \tag{4.1}$$

where

$$H=H_{ee}+H_{ei}+H_{ii}$$

and

$$H_{ee}=\sum_i \frac{p_i^2}{2m}+\sum_{i>j}\frac{e^2}{|\vec{x}_i-\vec{x}_j|}\ , \tag{4.2}$$

$$H_{ei}=\sum_{i,\alpha} v_{ps}(\vec{x}_i-\vec{R}_\alpha)\ , \tag{4.3}$$

$$H_{ii}=\sum_\alpha \frac{P_\alpha^2}{2M}+\tfrac{1}{2}\sum_{\alpha\neq\alpha'}\frac{Z^2e^2}{|\vec{R}_\alpha-\vec{R}_{\alpha'}|}+\sum_\alpha W_{\text{ext}}(\vec{R}_\alpha)\ . \tag{4.4}$$

Here $\vec{p}_i$ and $\vec{P}_\alpha$ represent the momenta of the ith electron and the αth ion, m and M are the electronic and ionic masses, e is the electronic charge, Z is the ionic valence, $\vec{x}_i$ and $\vec{R}_\alpha$ are the electronic and ionic coordinates, and v_{ps} is the bare electron-ion interaction, assumed to be represented by an energy-independent local pseudopotential.

If we take the ions to be classical and make the adiabatic approximation, the partition function in (4.1) can be rearranged so that the electronic trace is taken first and involves only that part of the Hamiltonian which depends on electronic coordinates. Thus we obtain

$$\begin{aligned}F=-k_BT\ln \text{Tr}_{\text{ion}}&\exp(-H_{ii}/k_BT)\\ &\times\text{Tr}_e\exp[-(H_{ei}+H_{ee})/k_BT]\end{aligned} \tag{4.5}$$

in which the trace over the electronic coordinates has the following simple interpretation:

$$\text{Tr}_e\exp[\ ]=\exp(-F'/k_BT)\ , \tag{4.6}$$

where F' is the electronic free energy corresponding to an interacting electron gas moving in an external potential defined by $H_{ei}+H_{ee}$. Thus the calculation of the free energy of the inhomogeneous liquid metal is broken into two separate problems: the first is to find the free energy of an electron gas in an external potential defined by the ions in a given configuration, and the second is to obtain the ionic free energy given that of the electrons, which will then act as an effective screening potential for the ions. The situation is analogous to that of a *homogeneous* liquid metal, but complicated by the reduced symmetry associated with the presence of the surface.

In order to calculate F' approximately, we must make the same assumption that is needed in the theory of homogeneous liquid metals: The electron-ion interaction must be assumed to be weak, so that a coupling-constant expansion can be carried out. To this end we write

$$H_{ei}=\int n_e(\vec{x})v_{ps}(\vec{x}-\vec{x}')n_{\text{ion}}(\vec{x}')d\vec{x}\,d\vec{x}'\ , \tag{4.7}$$

where $n_e(\vec{x})$ and $n_{\text{ion}}(\vec{x}')$ are the electronic and ionic density *operators*. Next we set

$$H_{ei}+H_{ee}=H_0+V\ , \tag{4.8}$$

where

$$\begin{aligned}H_0&=H_{ee}+\int n_e(\vec{x})v_{ps}(\vec{x}-\vec{x}')\bar{n}_{\text{ion}}(\vec{x}')d\vec{x}\,d\vec{x}'\ ,\\ V&=\int n_e(\vec{x})v_{ps}(\vec{x}-\vec{x}')[n_{\text{ion}}(\vec{x}')-\bar{n}_{\text{ion}}(\vec{x}')]d\vec{x}\,d\vec{x}'\ ,\end{aligned} \tag{4.9}$$

and $\bar{n}_{\text{ion}}(x)$ is some *nonuniform* reference ionic number density which can be chosen in any convenient fashion. V is the perturbation and represents the deviation of the actual ionic potential acting on the electrons in a given ionic configuration from the "mean" potential corresponding to $\bar{n}_{\text{ion}}(x)$. H_0 is the Hamiltonian for an interacting electron gas in the external potential corresponding to $\bar{n}_{\text{ion}}(x)$. The free energy F' is then given by the coupling-constant integral

$$F'\equiv F'(1)=F'(0)+\int_0^1\frac{dF'}{d\lambda}d\lambda\ , \tag{4.10}$$

where $F'(\lambda)$ is the free energy corresponding to the Hamiltonian $H_0+\lambda V$. $F'(0)$ is the Helmholtz free energy corresponding to the Hamiltonian H_0 and may be written (using the Hohenberg-Kohn-Sham-Mermin theorems for an interacting electron gas in an external potential)

$$\begin{aligned}F'(0)=F_{k\text{xc}}&[\bar{n}_e(\vec{x})]\\ &+\tfrac{1}{2}\int \bar{n}_e(\vec{x})\frac{e^2}{|\vec{x}-\vec{x}'|}\bar{n}_e(\vec{x}')d\vec{x}\,d\vec{x}'\\ &+\int \bar{n}_e(\vec{x})v_{ps}(\vec{x}-\vec{x}')\bar{n}_{\text{ion}}(\vec{x}')d\vec{x}\,d\vec{x}'\ ,\end{aligned} \tag{4.11}$$

where $F_{k\text{xc}}[\bar{n}_e(\vec{x})]$ represents the free energy (kinetic, exchange, and correlation energy plus entropy term) of an interacting electron gas of density $\bar{n}_e(\vec{x})$, and $\bar{n}_e(\vec{x})$ is the electronic density corresponding to the external potential produced by $\bar{n}_{\text{ion}}(\vec{x}')$. The terms in (4.10) can be computed by the standard methods used by Lang and Kohn[6] for a step-function ionic density and by Lu and Rice[16] for a monotonically decreasing ionic density.

The second term in (4.10) cannot, of course, be evaluated exactly even for a homogeneous liquid metal, and certainly not for an inhomogeneous one. We use a version of linear-response theory to get an approximate result. In explicit form the integral in (4.10) is

$$\int_0^1 d\lambda\langle V\rangle_\lambda\ , \tag{4.12}$$

where V is given by (4.9) and $\langle\ \rangle_\lambda$ denotes an average calculated with respect to a Hamiltonian $H_0+\lambda V$. Writing

$$\begin{aligned}\int_0^1 d\lambda\langle V\rangle_\lambda=\int_0^1 d\lambda&\langle n_e(\vec{x})\rangle_\lambda v_{ps}(\vec{x}-\vec{x}')\\ &\times\delta n_{\text{ion}}(\vec{x}')d\vec{x}\,d\vec{x}'\ ,\end{aligned} \tag{4.13}$$

where $\delta n_{\text{ion}}(\vec{x}')=n_{\text{ion}}(\vec{x}')-\bar{n}_{\text{ion}}(\vec{x}')$, we can formally write $\langle n_e(\vec{x})\rangle_\lambda$ to first order in λV:

$$\langle n_e(\vec{x})\rangle_\lambda = \bar{n}_e(\vec{x}) + \lambda \int d\vec{x}''d\vec{x}'''\{\chi_{ee}[\vec{x},\vec{x}'';\bar{n}_e(\vec{x})]v_{ps}(\vec{x}''-\vec{x}''')\delta n_{\rm ion}(\vec{x}''')\} \; , \tag{4.14}$$

where we have used the explicit definition of V and $\chi_{ee}[\vec{x},\vec{x}';\bar{n}_e(\vec{x})]$ represents the density response function of a *nonuniform* electron gas of unperturbed density $\bar{n}_e(\vec{x})$. The form (4.14) follows at once from the definition of the response function, as given, for example (for a *uniform* system), in Pines and Nozières.[9] Carrying out the coupling-constant integral gives finally to lowest order,

$$\begin{aligned} F' = F_{k\rm xc}[\bar{n}_e(\vec{x})] &+ \tfrac{1}{2}\int \bar{n}_e(\vec{x})V_{ee}(\vec{x}-\vec{x}')\bar{n}_e(\vec{x}')d\vec{x}\,d\vec{x}' + \int \bar{n}_e(\vec{x})v_{ps}(\vec{x}-\vec{x}')n_{\rm ion}(\vec{x}')d\vec{x}\,d\vec{x}' \\ &+ \tfrac{1}{2}\int \delta n_{\rm ion}(\vec{x})V_{\rm scr}[\vec{x},\vec{x}';\bar{n}_e(\vec{x})]\delta n_{\rm ion}(\vec{x}')d\vec{x}\,d\vec{x}' \; , \end{aligned} \tag{4.15}$$

where

$$V_{\rm scr}(\vec{x},\vec{x}';\bar{n}_e) = \int d\vec{x}''d\vec{x}'''v_{ps}(\vec{x}-\vec{x}'')v_{ps}(\vec{x}'-\vec{x}''')\chi_{ee}(\vec{x}'',\vec{x}''';\bar{n}_e) \tag{4.16}$$

is the screening contribution to the effective ion-ion interaction. The factor of $\frac{1}{2}$ comes from the coupling-constant integration, and the result (4.15) is nothing more than the analog for nonuniform systems of the usual structural expansion for liquid metals in a particular ionic configuration. We note also that (4.15) is fully applicable to *solid* metals with a surface, provided that the ions are then arranged in a suitable lattice. The extra difficulty associated with the liquid state is the need to average over ionic configurations. Both solid and liquid will require calculating (or approximating) the difficult nontranslationally invariant response function χ_{ee}. (Chakravarty *et al.*[28] and Rose and Dobson[24] have successfully used such response functions for molecular hydrogen and discrete-ion corrections to the planar uniform background model of metal surfaces, respectively. Our approach bears a close resemblance to recent work by Foiles and Ashcroft[29] who use standard electron density-functional methods to calculate the $\bar{n}_e$ corresponding to an ion profile $\bar{n}$, and use the inhomogeneous response functions $\chi_{ee}[\bar{n}_e(\vec{x})]$ to calculate discrete-ion corrections; they then use a liquid-state variational principle to find the optimal $n_i(\vec{x})$.)

Given F' for a particular ionic configuration, the remainder of the calculation is a liquid-state problem, i.e., it involves determining the arrangement of the ions, given the forces they sense. The effective ionic potential energy is

$$V_{\rm eff}(\{\vec{R}_\alpha\}) = F' + \tfrac{1}{2}\sum_{\alpha\neq\alpha'}\frac{Z^2e^2}{|\vec{R}_\alpha-\vec{R}_{\alpha'}|} + \sum_\alpha W_{\rm ext}(\vec{R}_\alpha) \; , \tag{4.17}$$

which can be decomposed into one-body and two-body terms using Eqs. (4.15), (4.16), and the relation $\delta n_{\rm ion}(\vec{x}) = n_{\rm ion}(\vec{x}) - \bar{n}_{\rm ion}(\vec{x})$. It is easily found that

$$V_{\rm eff}(\{\vec{R}_\alpha\}) = \tfrac{1}{2}\sum_{\alpha\neq\alpha'} W^{(2)}_{\rm eff}(\vec{R}_\alpha,\vec{R}_{\alpha'}) + \sum_\alpha W^{(1)}_{\rm eff}(\vec{R}_\alpha) \tag{4.18}$$

plus terms which are independent of ionic position. The pair potential $W^{(2)}_{\rm eff}(\vec{R}_\alpha,\vec{R}_{\alpha'})$ takes the form

$$W^{(2)}_{\rm eff}(\vec{R}_\alpha,\vec{R}_{\alpha'}) = \frac{Z^2e^2}{|\vec{R}_\alpha-\vec{R}_{\alpha'}|} + V_{\rm scr}[\vec{R}_\alpha,\vec{R}_{\alpha'};\bar{n}_e(\vec{x})] \; , \tag{4.19}$$

where $V_{\rm scr}$ is defined in (4.16). The one-body term can be written (after some rearrangements)

$$W^{(1)}_{\rm eff}(\vec{R}_\alpha) = W_{\rm ext}(\vec{R}_\alpha) + W_{\rm att}(\vec{R}_\alpha) + W_{\rm pol}(\vec{R}_\alpha) \; , \tag{4.20}$$

$$\begin{aligned} W_{\rm att}(\vec{R}_\alpha) = \int d\vec{x}[&V_{\rm scr}(\vec{R}_\alpha,\vec{x};\bar{n}_e)\bar{n}_{\rm ion}(\vec{x}) \\ &+ v_{ps}(\vec{R}_\alpha-\vec{x})\bar{n}_e(\vec{x})] \; , \end{aligned} \tag{4.21}$$

$$W_{\rm pol}(\vec{R}_\alpha) = V_{\rm scr}[\vec{R}_\alpha,\vec{R}_\alpha;\bar{n}_e(\vec{x})] \; . \tag{4.22}$$

Each of the terms in (4.20) has a relatively simple physical meaning: $W_{\rm ext}$ is the external potential acting on the ions and $W_{\rm att}$ is an effective one-body attractive potential which arises indirectly from an interaction between ions attempting to escape the liquid metal and the electrons and other ions left behind. It tends to keep the ions in the liquid phase and will presumably (although this could only be confirmed by detailed calculation) behave rather like a soft wall of finite height for the ions. The last term, $W_{\rm pol}$, is a self-interaction term which arises from the anisotropy of the screening cloud around an ion in the surface region. (In a uniform system $W_{\rm pol}$ would be position independent.) The existence of such *one-body* potentials, tending to keep ions from escaping from a liquid metal, is special to metallic fluids: They do not occur in simple *insulating* liquids such as Ar. They have been previously suggested by D'Evelyn and Rice[4] but are here proved to follow naturally from an extension of the structural expansion to liquid-metal surfaces.

Note that the treatment given above does not explicitly treat the metal-insulator transition, i.e., the vapor limit is not given correctly. We do not anticipate that this omission will have much *quantitative* importance in liquid metals since, as previously indicated, the properties of the surface are most likely determined mostly by the denser (liquid) phase far from the critical point.

V. SUMMARY AND CONCLUSIONS

We have presented above a brief analysis of the density-functional theory for inhomogeneous classical fluids generalized to a liquid metal. It was demonstrated that explicit reference to electronic degrees of freedom could be eliminated, although the second electronic fluid constituent is implicit in the response functions which occur in the formal expression for the free energy of the inhomogeneous system.

The inhomogeneous contribution to the free energy was described by a gradient approximation. This allowed the nonuniform liquid metal to be studied by means of a set of approximations widely used for *uniform* liquid metals. With the use of a reasonable estimate of the gradient-term coefficient based on a mean-spherical-like approximation and a simple variational form for the ionic density profile, the surface tension and surface width were calculated for a number of simple metals.

Agreement with experiment for the surface tension τ at melting was very good for the alkalis. The less satisfactory results for Zn and Al served as motivation for a general, approximate scaling form for the surface tension at melting. The scaling theory agrees reasonably well with experiment for a large variety of metals and is at least as satisfactory as existing parametrizations of τ in terms of bulk liquid quantities.

It should be stressed that the only inputs to the full theory of Sec. II are a parameter characterizing the range of the electron-ion pseudopotential and the bulk liquid density. The remarkable quality of the theoretical predictions for the liquid alkalis suggest several things:

(i) Surface tension seems likely to be insensitive to possible oscillations[4,30] of the ionic density profile in light of our good results from the simple gradient theory (which involves a monotonic profile) above.

(ii) Presence of a metal-insulator transition as one traverses the liquid/vapor interface seems to have little effect on the energetics of the surface, at least at temperatures where the coexisting phases are of very different densities.

(iii) Density-functional formalism used here is probably adequate to describe liquid-metal surfaces, any inaccuracies in the polyvalent metals arising from inadequately known inputs rather than fundamental shortcomings of the theory.

Finally, to improve upon the simple formalism employed above so as to permit explicit discussion of electronic properties of the surface, the usual linear-response description of a uniform liquid metal was generalized to allow for a nonuniform *reference* electron-ion system about which the usual perturbation theory is used. A judicious rewriting of the terms generated allowed us to isolate both one- and two-body forces which are peculiar to liquid-metal interfaces. The former may be responsible for the "hard-wall"-like interactions discussed by D'Evelyn and Rice.[4]

Note added in proof. D. Stroud and M. Grimson (unpublished) have recently recalculated the surface tensions of liquid Al and Na, using the full density-functional formalism [Eqs. (2.16), (2.19), and (2.20)] rather than the gradient approximation, and a slightly different prescription for $C(r)$. The resulting surface tension for Al is in much better agreement with experiment than that obtained within the gradient approximation; the surface tension for Na is reduced slightly below that predicted by the gradient approximation, but is still within 20% of experiment. In both cases the predicted surface profile has weak ionic density oscillations superimposed on a nearly steplike background.

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[1] See, for example, N. W. Ashcroft and D. Stroud, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1978), Vol. 33, pp. 1 ff.

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[9] See, for example, D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966), Vol. I, Sec. 2.3.

[10] In fact, Eq. (2.9) follows from Eq. (2.7) if one assumes the electrons respond linearly via the electron-ion interaction to an adiabatically moving arbitrary classical distribution $\delta n_i(q)$. The assumed smallness of $\delta n(r)$ assures the validity of linear response. This viewpoint does not require invoking a fictitious external potential that couples differently to electrons and ions. Trigger [Phys. Lett. 56A, 325 (1976)] has shown that the relation between δn_e and δn_i obtained from the general expression (2.8) is equivalent to simple linear response for a weak pseudopotential.

[11] This is true for $\vec{r}\neq 0$; in general, using (2.9)–(2.11), $G(q)=(k_BT/\bar{n})[1-\bar{n}C(q)]$.

[12] We have used the Hubbard dielectric function as modified by Geldart and Vosko [D. J. W. Geldart and S. H. Vosko, Can. J. Phys. 44, 2137 (1966); see also P. Vashishta and K. S. Singwi, Phys. Rev. B 6, 875 (1972); 6, 883 (1972)].

[13] At $n=n_{\text{bulk}}$ the quantity $F^*/N=F/N-E_0/N$ (since E_0 is independent of η) is minimized with respect to η. Next $r_c^{E_0}$ is obtained by requiring that $P=-(\partial F/\partial V)=0$ at $n=n_{\text{bulk}}$; the derivative

$$P=n^2\left[\frac{\partial}{\partial n}\left[\frac{F^*}{N}\right]+\frac{\partial}{\partial \eta}\left[\frac{F^*}{N}\right]\frac{\partial \eta}{\partial \rho}+\frac{\partial E_0}{\partial n}\right]=0$$

is evaluated numerically taking care to preserve the local electrical neutrality of the hard-sphere *reference* system characterized by packing fraction η. The value of $r_c^{E_0}$ satisfying this equation is fixed thereafter for all densities, and the η's minimizing F/N for five other densities are found as described in the text.

[14] Had we made the gradient approximation at the level of Eq. (2.15), the quantity K' would have been a constant and $\bar{n}$ would have been *precisely* $\bar{n}=\frac{1}{2}(n_l+n_v)$ with our choice (3.15). This choice of $\bar{n}$ is thus not an *ad hoc* one; this is the probable explanation for the observation of Mon and Stroud, Phys. Rev. Lett. 45, 819 (1980), that is was "crucial" to calculate $C(r,n)$ at $n=\frac{1}{2}n_l$.

[15] It appears that this is so in our case because the fundamental length scale in the problem is r_c (not σ in K' which is defined via k_BT). It may be seen that the quantity w/r_c is roughly a constant for all cases calculated; for the alkalis, it is very close to unity. See also the references in Ref. 2 for a discussion of this apparently general weakness of pseudoatom theories. Recent measurements by Sluis, D'Evelyn, and Rice [J. Chem. Phys. 78, 1611 (1983)] however, indicate a 10—90% width for the Cs vapor/liquid interface of 3.5—4.0 Å (fit with a tanh profile), in reasonable agreement with our prediction (see Table II) of 3.0 Å ($=2.1972w$). Our surface width predictions for Na and Cs are also close to the pseudoatom predictions of D'Evelyn and Rice, J. Chem. Phys. 78, 5225 (1983). We thank Dr. D'Evelyn for the above information. (We also note that our results for Na for dw/dT are of the wrong sign.)

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[18] See the review by B. C. Allen, in *Liquid Metals: Chemistry and Physics,* edited by S. Z. Beer (Dekker, New York, 1972), Sec. VII, p. 161.

[19] Within the gradient formalism used here for a monotonic ion profile such as we have used in Eq. (3.14), a simultaneous increase in the gradient contribution B and reduction in the local free-energy term A by the same factor would, for the alkalis, increase the surface width while keeping the surface tension constant (and in good agreement with experiment). For the polyvalents a reduction in the gradient coefficient will clearly reduce τ. It is also possible that a careful account of the vapor phase would broaden the interface width.

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[27] This approach would be entirely consistent with the procedure of Sec. II; see Ref. 10. The system as a whole (electrons and ions) is *globally* electrically neutral and our hard-sphere *reference* system is *locally* neutral. But the actual ionic and electronic density profiles calculated from this method will not nest in general; as a rule the electron profile will be more diffuse. We have refrained from calculating the surface dipole moment because of the narrowness of our variationally obtained ionic profiles.

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