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# Theory of the interfacial tension between liquid metals

K. K. Mon* and D. Stroud
Department of Physics, The Ohio State University, Columbus, Ohio 43210
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We present a method for calculating the interfacial tension between two immiscible liquid metals with use of an ionic density-functional formalism in conjunction with pseudopotential theory. The method is applied to $Li_{1-x}Na_x$ at 452 K. The resulting tension is found to be 10.5 dyn/cm, much smaller than the free-surface tensions of the constituents, and the width of the interfacial profile is calculated to be about 6.7 Å.

The interfacial tension between immiscible metals is a parameter which plays a large role in many metallurgical processes.[1] It helps control the rate of spinodal decomposition of immiscible metals, for example, as was first emphasized by Cahn[2] and later discussed by Langer and co-workers.[3] Immiscible metals may also be quenched from the liquid state to form technologically important composites. The morphology of these composites depends strongly on the interfacial tension.[4] Moreover, besides the free energy itself, the width of the interface is of interest as a region over which the composition of the alloy changes substantially.

In this paper we present apparently the first microscopic calculation of the interfacial tension between two liquid metals. Our calculation is based on the well-known ionic density-functional formalism used previously to treat the free surface of a liquid metal in equilibrium with its vapor,[5] and used here (in suitably generalized form) to treat mixtures of liquid metals. The calculation allows one to extract not only the interfacial tension but also the thickness of the interface and the temperature dependence of the surface tension in a simple manner. Since the density-functional formalism in our approximation makes use of *bulk* properties to calculate *surface* ones, it may well be suited for parametrization and extrapolation to as yet unmeasured interfaces. Finally, although this work is directed towards liquid metals, it may help to estimate the electronic part of the surface tension between *solid* intermetallics. (However, this tension will also be substantially influenced by elastic energies arising from atomic size mismatch.)

The basis of our work is the following expression for the Helmholtz free energy $F$ of an *inhomogeneous* liquid alloy:

$$F[n_1(z),n_2(z),T]=\int_{-\infty}^{\infty} f(n_1(z),n_2(z),T)dz+\sum_{i,j=1,2}^{2}\int_{-\infty}^{\infty} K_{ij}(n_1,n_2,T)\frac{dn_i}{dz}\frac{dn_j}{dz}dz\ . \tag{1}$$

Here $n_1(z)$ and $n_2(z)$ are the ionic number densities of species 1 and 2 of the alloy at position $z$, $f(n_1,n_2,T)$ is the Helmholtz free-energy density of a hypothetical alloy of densities $n_1$ and $n_2$ at temperature $T$, and the gradient coefficient $K_{ij}(n_1, n_2,T)$ is defined by

$$K_{ij}(n_1,n_2,T)=\frac{k_BT}{12}\int_0^{\infty} r^2C_{ij}(r;T)d^3x\ , \tag{2}$$

$C_{ij}(r;T)$ being the Ornstein-Zernike direct correlation functions of the alloy $(i,j=1,2)$. Equations (1) and (2) are the generalization of the one-component ionic density-functional theory used in Ref. 5, in the limit in which the partial densities are slowly varying on a scale set by the range of $C_{ij}$.

Note that the conduction electrons are *not* omitted from (1) by considering the alloy to consist of two components only; they are properly included within the adiabatic approximation.

The interfacial tension $\tau$ between two immiscible phases $A$ and $B$, at pressure $P$ and temperature $T$, takes the following form:

$$\tau=\int_{-\infty}^{\infty}(f-\mu_1n_1-\mu_2n_2+P)dz+\sum_{ij}\int_{-\infty}^{\infty}K_{ij}\frac{dn_i}{dz}\frac{dn_j}{dz}dz\ . \tag{3}$$

Here $\mu_i(i=1,2)$ is the chemical potential of the $i$th alloy component, and $P$ is the pressure, which by the Gibbs-Duhem relation is the negative of the grand free energy $\Omega$ per unit volume. In the limits $z=\pm\infty$, the densities approach $(n_{1A},n_{2A})$ and $n_{1B},n_{2B})$, respectively, these being partial densities of the two immiscible alloy phases. Note that the integrands in (3) vanish at $z=\pm\infty$, so that $\tau$ is the *extra* grand free energy per unit area required to form an interface, consistent with its thermodynamic definition. To apply (3) to the calculation of the interfacial tension of a real alloy, one minimizes (3) with respect to all possible surface profiles defined by the two partial densities. This procedure gives not only the surface tension but also the density profile across the interface.

We have tested the theory described above by applying it to liquid Li and Na in equilibrium. This is an alloy which has a miscibility gap, the components being mutually soluble in all proportions above $T\sim 590$ K but phase-separating at lower temperatures. Since this miscibility gap is adequately described by the equilibrium theory of homogeneous liquid alloys,[6] it is a natural choice for testing a theory of interfacial tension.

The free-energy density and correlation functions appearing in Eq. (1) and (2) were evaluated by means of standard approximations in the theory of homogeneous liquid metals. For $f(n_1,n_2,T)$ a structural expansion was used, in which the electron-ion interaction was included to second order as described in Ref. 6. Structure-dependent terms in the internal energy were evaluated using Percus-Yevick structure factors for a mixture of hard spheres of different diameters.[7] The entropy was taken to be that of a similar hard-sphere mixture, as fitted by Carnahan and Starling to computer simulations. The hard-sphere diameters $\sigma_1$ and $\sigma_2$ were taken to be concentration-independent and equal to the values shown in Table I. They were chosen to satisfy the condition $V_{ii}(\sigma_i)=\frac{3}{2}k_BT$,[7] where $V_{ii}$ is the standard screened interionic pair potential for the $i$th species at its equilibrium liquid density. This is a typical distance of closest approach that would be expected of an ion with a kinetic energy $\frac{3}{2}k_BT$. While a variational calculation performed at each concentration and temperature would give a slightly more accurate free energy, the present method is adequate. Empty-core pseudopotentials were used for simplicity and the Hartree terms in the free energy were chosen to satisfy the zero-pressure requirement $(\partial F/\partial v)_T=0$ at the equilibrium atomic volumes of the pure metals at melting ($F$ being the Helmholtz free energy per ion). The resulting values of the various parameters used in the calculation are listed in Table I. Finally, for the correlation functions, we used the approximation

$$C_{ij}(r)=C_{ij}^{\mathrm{hs}}(r)\quad\text{for } r<\sigma_{ij},$$
$$C_{ij}(r)=-V_{ij}(r)/k_BT\quad\text{for } r>\sigma_{ij}\ ,$$

where $C_{ij}^{\mathrm{hs}}(r)$ is the Percus-Yevick hard-sphere correlation function, $V_{ij}(r)$ is the (density-dependent) screened interionic potential between ions of species $i$ and $j$ as calculated using Hubbard polarization corrections to Lindhard screening, and $\sigma_{ij}=(\sigma_i+\sigma_j)/2$.

To calculate the surface tension, we minimized (3) with respect to the one-parameter surface profile defined by

$$\begin{aligned} x(z)&=\frac{x_1+x_2}{2}+\frac{x_1-x_2}{2}\tanh(\beta z)\ ,\\ n_1(z)&=[1-x(z)]n(z)\ ,\\ n_2(z)&=x(z)n(z)\ ,\\ n(z)&=\{x(z)v_2+[1-x(z)]v_1\}^{-1}\ , \end{aligned}\tag{4}$$

$v_1$ and $v_2$ being the atomic volume of components 1 and 2, respectively. This is the obvious generalization of the hyperbolic tangent profile which is the *exact* solution for interfaces described by free-energy functionals of the Ginzburg-Landau form.[6] For the present functional it does not, of course, provide an exact minimization, but it does ensure that the atomic volume of the alloy is a linear function of concentration (Vegard's law) as is experimentally well obeyed for alloys of alkali metals.[8]

TABLE I. Values of the various parameters used in evaluating $\tau$. All numbers are in atomic units. $\sigma_{\mathrm{Li}}$ and $\sigma_{\mathrm{Na}}$ are the hard-sphere diameters, $r_c^{\mathrm{Li}}$ and $r_c^{\mathrm{Na}}$ the empty-core radii, $\alpha_{\mathrm{Li}}$ and $\alpha_{\mathrm{Na}}$ the Hartree coefficients [as defined in Ashcroft and Stroud (Ref. 6), Eq. (4.2e)], and $v_{\mathrm{Li}}$ and $v_{\mathrm{Na}}$ the equilibrium atomic volumes.

| $\sigma_{\mathrm{Li}}$ | $\sigma_{\mathrm{Na}}$ | $r_c^{\mathrm{Li}}$ | $r_c^{\mathrm{Na}}$ | $\alpha_{\mathrm{Li}}$ | $\alpha_{\mathrm{Na}}$ | $v_{\mathrm{Li}}$ | $v_{\mathrm{Na}}$ |
|---|---|---|---|---|---|---|---|
| $5.11a_0$ | $5.795a_0$ | $1.4a_0$ | $1.69a_0$ | $10.94a_0^2$ | $17.94a_0^2$ | $151.6a_0^3$ | $278a_0^3$ |

With the choice (4), $f-\sum_i \mu_i n_i + P$ becomes a function of a single variable (total number density $n$ or, equivalently, concentration $x$ of Na), and is plotted in Fig. 1 at 452 K, slightly above the melting temperature of Li. The equilibrium concentrations of the two coexisting phases at this temperature are calculated to be 15% and 85% Na, and the height of the free-energy density barrier separating the two phases is only 0.1 K/a.u.$^3$). Such an energy is certainly far smaller than accuracy of the pseudopotential method. But simple estimates, based on the regular solution model, show that when the mutual solubility of the alloy constituents is ~15%, the free-energy barrier must be only about 3% of the heat of formation $H$ of an equiatomic alloy from its constituents. $H$ is estimated by Hafner[9] to be of order 5 K/a.u.$^3$), and so the barrier calculated here is not unreasonable.

The minimization with respect to $\beta$ is readily carried out with the help of a change of integration variables from $z$ to $n$, and the interfacial tension and width are given by

$$\tau = 2\sqrt{ab} \ ,$$

$$\beta = \sqrt{a/b} \ ,$$

$$a = \left[\frac{\Delta n}{2}\right]^{-1} \int_{n_<}^{n_>} \Omega(n) \left[1 - \frac{4(n-\bar{n})^2}{(\Delta n)^2}\right]^{-1} dn \ , \quad (5)$$

$$b = \frac{\Delta n}{2} \int_{n_<}^{n_>} K_{\text{eff}}(n) \left[1 - \frac{4(n-\bar{n})^2}{(\Delta n)^2}\right] dn \ ,$$

$$K_{\text{eff}} = [K_{11}(\Delta n_1)^2 - 2K_{12}\,|\Delta n_1|\,|\Delta n_2| + K_{22}(\Delta n_2)^2]/(\Delta n)^2 \ .$$

Here $n_<$ and $n_>$ are the ionic number densities of the two coexisting phases, $\Delta n_1$ and $\Delta n_2$ are the differences between the two corresponding partial-number densities,

$$\bar{n} = (n_< + n_>)/2$$

and

$$\Omega(n) = f - \sum_i \mu_i n_i + P \ .$$

$\Omega(n)$ is to be computed at the density $n$ which satisfies Vegard's law. In evaluating (5), we assumed, purely for convenience, that $K_{\text{eff}}(n)$ is density-independent and equal to its value at $n=\bar{n}$. The resulting values for $K_{\text{eff}}$, $a$, $b$, $\tau$, and $w=\beta^{-1}$ are listed in Table II, where we also list for comparison the surface tensions of pure liquid Li and Na at melting.

The results shown in Table II show some striking differences from the corresponding surface behavior of pure metals. In particular, the interfacial tension is about an order of magnitude lower, although surface *width* $w$ is about the same as the corresponding calculated values for pure liquid metals. These features may be understood from the fact that an intermetallic interface is less "abrupt," with a more indistinct change of properties, than a metallic liquid-vapor boundary. Thus, one expects in the former case to have a smaller contribution from both the homogeneous and gradient part of the free-energy ($a$ and $b$, respectively). [See Eq. (5).] This results in much smaller energy but about the same profile width as in the pure case.

The magnitude of both $\tau$ and $\beta$ depend sensitively on the height $\Delta f$ of the free-energy barrier shown in Fig. 1. If we make the extremely over-simplified approximation

$$\Omega(n) = \Delta f (n_> - \bar{n})(\bar{n} - n_<)/(\Delta n/2)^2 \ ,$$

the coefficient $a$ can be calculated analytically from (5). The result is $a = 2\Delta f = 0.24$ K/(a.u.)$^3$, within 30% of the value calculated by numerical integration of the actual free-energy barrier. Also, combining the first two equations of (5) gives

$$\beta\tau = 2a \sim 4\Delta f \ ,$$

which provides a direct measure of the product of the interfacial tension and the inverse-width parameter $\beta$, independent of the difficult-to-calculate gradient coefficient. While the free-energy barrier cannot be directly measured, at low temperatures it approaches the heat of formation per unit volume of an equiatomic alloy, which can be experimentally estimated by various means.[10]

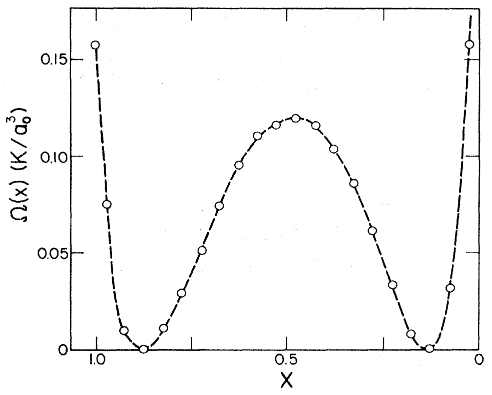

FIG. 1. Excess grand free-energy density $\Omega(x)$ as a function of the concentration $x$ of Na at $T=452$ K.

TABLE II. Values of the various coefficients described in the text. $a$, $b$, and $K_{\text{eff}}$ are defined in Eq. (5), $\tau$ is the interfacial tension in liquid $\text{Li}_{1-x}\text{Na}_x$ at 452 K, $w$ is the half-width of the interfacial profile, $\tau_{\text{Na}}$ and $\tau_{\text{Li}}$ are the free-surface tensions, and $w_{\text{Na}}$ and $w_{\text{Li}}$ are the half-width of the pure liquid metals at melting (Ref. 5). The value in parentheses for $a$ is the number calculated using the approximation $\Omega(n)=\Delta f(n_{>}-\bar{n})(\bar{n}-n_{<})/(\Delta n/2)^2$.

| $a$ | $b$ | $K_{\text{eff}}$ | $\tau$ | $w=\beta^{-1}$ | $\tau_{\text{Na}}$ | $\tau_{\text{Li}}$ | $w_{\text{Na}}$ | $w_{\text{Li}}$ |
|---|---|---|---|---|---|---|---|---|
| $0.17K/a_0^3$<br>(0.24) | $6.7K/a_0$ | $0.43\times10^7$ $Ka_0^5$ | 10.5 dyn/cm | $6.29a_0$ | 191 dyn/cm | 398 dyn/cm | $6.39a_0$ | $5.11a_0$ |

This simple estimate may be useful in obtaining relationships between $\tau$ and $\beta$ in many binary systems, not just liquid metals.

The value of 10.5 dyn/cm cannot, at present, be directly compared with experiment. We note, however, that the HgGa system has interfacial tension of only 37 dyn/cm, far smaller than the free-surface tensions of either component separately (by a factor of around 20). Thus, the small value we find for $\text{Li}_x\text{Na}_{1-x}$ is not unreasonable.

To conclude, we have carried out the first microscopic calculation of the interfacial tension between two immiscible liquid metals. The results are of interest, not only in themselves, but also as a guide to future experimental and theoretical studies of interfaces, perhaps solid as well as liquid.

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*Permanent address: Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213.

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