Theory of the surface tension of liquid metal alloys

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We present a density-functional theory of the surface tension of liquid metal alloys. The theory is applied to miscible alloy Na$_x$K$_{1-x}$ and the results are similar to typical miscible alloys. The phenomenon of segregation of the low-surface-tension component to the surface is obtained with use of a simple hyperbolic tangent concentration profile. An estimation of the surface concentration is made within the monolayer surface model.

I. INTRODUCTION

It has long been known that the surface tension of most liquids is strikingly modified by the presence of a few low-surface-tension impurities. The modification consists of a dramatic drop in surface tension with impurity concentration, and occurs because the impurities tend to migrate to the surface, thereby lowering the free energy and the surface tension as well. The effect is of practical as well as fundamental importance. Certain liquid metals are difficult to maintain entirely free of impurities, and the strong impurity dependence means that measurements of the surface tension of the pure liquids are difficult to carry out with reliable accuracy. Moreover, certain convection processes ("Marangoni convection") are driven by surface-tension gradients parallel to the surface. If there is a gradient of impurity concentration $x$ parallel to the surface, and if $\tau$ is strongly dependent on $x$, then Marangoni convection may be quite important, and may indeed dominate the spatial distribution of liquid in a low-gravity environment such as an orbiting satellite, where gravity-driven convection processes are suppressed.

The purpose of this paper is to describe a method for calculating the surface tension of liquid metal alloys, which conspicuously shows both surface segregation and the associated dramatic drop of surface tension at low concentrations of the low-surface-tension impurity. The method of calculation consists of a generalization to alloys of the density-functional scheme used by Wood and Stroud$^1$ for monocomponent liquid metals. This scheme breaks the free energy of the liquid metal into a local part, involving a free-energy density, and a non-local portion, which is taken in the gradient approximation. In the present paper both the free-energy density and the gradient contribution are calculated from first principles, using approximations derived from a combination of pseudopotential theory and equilibrium statistical mechanics. The resulting calculation gives good results for the surface tensions of both pure liquid Na and pure liquid K (the two metals chosen as examples in this calculation). The surface tension of the alloys has not been measured, to our knowledge, but the depression of the surface tension of the alloy relative to a straight-line interpolation of those of the constituents is found to be clearly correlated with the degree of surface segregation.

There have been several previous theoretical attempts to deduce the existence of surface segregation from simple models. Moran-Lopez and Falicov$^2$ have calculated the composition and short-range order in the surface layer of a solid alloy within an Ising-like model, using the pair (or Bethe) approximation to solve the model. The parameters of the model were not, however, calculated from any fundamental theory but rather were taken as empirically determined quantities. Miedema$^3$ has suggested that the major driving force for surface segregation is the difference in the pure metal surface tensions, and has proposed empirical formulas for estimating the surface tension based on this observation. Telo de Gama and Evans$^4$ have calculated the surface tension of a binary Lennard-Jones fluid, using a model somewhat similar to our own, but for an insulating fluid. They found segregation of the smaller-surface-tension component when $x$ (the concentration of component of lower surface tension) is very small, but near $x = 1$ they found surface segregation of the component of larger surface tension, contrary to expectations. To our knowledge, no previous theoretical attempt has been made to calculate the surface tensions of liquid metal alloys.

The remainder of the paper is organized as follows. The formalism used in our calculations is outlined in Sec. II. The results are presented in Sec. III, following which is a brief discussion given in Sec. IV.

II. FORMALISM

A. Review of the density-functional approach for liquid metals

We are concerned with the surface tension of a liquid mixture with a free surface, and in equilibrium with its vapor. The thermodynamic states of the two phases in equilibrium with each other are then determined by the pressure $P$, the temperature $T$, and one of the two chemical potentials, $\mu_1$ and $\mu_2$, of the constituents (these parameters will determine the density of each constituent in each of the two phases). Under such conditions, the system will go into its state of lowest grand free energy $\Omega$, where $\Omega$ is defined by the relation
\[ \Omega(n_1(z), n_2(z), T) = F(n_1(z), n_2(z), T) - \mu_1 \int_{-\infty}^{\infty} n_1(z) dz - \mu_2 \int_{-\infty}^{\infty} n_2(z) dz. \]  

Equation (1) emphasizes that the two-phase system is inhomogeneous: it is appropriate to a situation where the surface is situated at \( z = 0 \), with the vapor phase in the half-space \( z < 0 \), the liquid at \( z > 0 \). The grand free energy is then a functional of the two ionic number densities, \( n_1(z) \) and \( n_2(z) \), both of which depend only on the coordinate perpendicular to the interface, since the surface is planar. The densities \( n_1(z) \) and \( n_2(z) \) are understood to be ensemble averages of the two ionic densities of the problem. By functional, of course, is meant a function of the functions \( n_1(z) \) and \( n_2(z) \).

If the form of the function \( F(n_1(z), n_2(z), T) \) is known, then the surface tension can be calculated from the relation

\[ F(n_1(x), n_2(x), T) = \int dxf(n_1(x), n_2(x), T) + \frac{k_B T}{4} \sum_{i,j=1}^{2} \int C_{ij}(x-x'; \vec{n}_i, \vec{n}_j, T)[n_i(x) - n_i(x')][n_j(x) - n_j(x')] dx dx', \]

where \( f(n_1, n_2) \) is the Helmholtz free-energy density of a homogeneous liquid mixture of densities \( n_1 \) and \( n_2 \) at temperature \( T \), and \( C_{ij}(r; \vec{n}_1, \vec{n}_2, T) \) is the so-called direct correlation function for a liquid mixture of suitable intermediate densities \( \vec{n}_1, \vec{n}_2 \), and temperature \( T \) (for a two-component liquid mixture, there are three such direct correlation functions since \( C_{ij} = C_{ji} \)). \( \vec{n}_1 \) and \( \vec{n}_2 \) are some suitable intermediate densities. The Fourier transforms of the direct correlation functions are, of course, related to the partial ionic structure factors, \( S_{ij}(k) \), which are defined below. As was shown by Wood and Stroud for a single-component liquid (the generalization to two components is obvious), Eq. (3) is exact for an inhomogeneous liquid, in the limit of small-magnitude density fluctuations of arbitrarily short wavelengths, although it becomes approximate for a system with a free surface, where the differences \( n_i(x) - n_i(x') \) became large. In the latter case, part of the approximation consists of deciding at what value of \( n_i \) to evaluate the correlation functions \( C_{ij}(x-x') \); this approximation is of necessity somewhat arbitrary.

For a single-component liquid metal, Wood and Stroud showed that Eq. (3) remains valid to the same degree as for an insulating fluid, provided that the free-energy densities and correlation functions are taken as those of a liquid metal, including the effects of the free electron gas. The same is true for a liquid metal alloy.

If the partial ionic densities of the liquid mixture are sufficiently slowly varying, it may be reasonable to replace the nonlocal kernel [the second term of Eq. (3)] by a local-gradient approximation. In that case, a simple extension of the results of Ref. 1 gives the following form for the free-energy functional in the case of a planar surface perpendicular to the \( z \) axis:

\[ F(n_1(z), n_2(z), T) = \int_{-\infty}^{\infty} f(n_1(z), n_2(z), T) dz + \sum_{i,j=1}^{2} \int_{-\infty}^{\infty} K_{ij}(\vec{n}_1, \vec{n}_2, T) \times \frac{dn_i(z)}{dz} \frac{dn_j(z)}{dz} dz, \]

where the kernel functions \( K_{ij}(\vec{n}_1, \vec{n}_2, T) \) are given by

\[ K_{ij}(\vec{n}_1, \vec{n}_2, T) = k_B T \frac{C_{ij}(r; \vec{n}_1, \vec{n}_2, T)}{12} dr. \]

As in the full density-functional theory, this expression is exact through second order in the density deviation, \( n_i(z) - n_i^0 \), with respect to some unperturbed uniform density \( n_i^0 \), and with the further approximation of slow spatial variation of density.

Equations (2) and (3), or (2) and (4), give a complete prescription for calculating the surface tension of a liquid mixture (or liquid alloy), given a way of computing the free-energy densities and correlation functions of the corresponding homogeneous liquid. This ionic density-functional scheme is the analog, for classical ions, of the electronic density-functional scheme introduced by Hohenberg and Kohn for calculating the ground-state properties of an inhomogeneous electron gas.

B. Free-energy density and functions
for a mixture of liquid metals

We are concerned in this paper with a mixture of nearly-free-electron liquid metals, that is, metals in which
the electron-ion interaction can be treated satisfactorily within second-order perturbation theory. In that case, the Helmholtz free-energy perturbation is adequately approximated as follows:

\[
f = nF,
\]

\[
F = E_M + E_{BS}^{(2)} + E_{EG} + E_0 + \frac{1}{2} k_B T - T\mathcal{S},
\]

where \( F \) is the Helmholtz free energy per ion and the individual terms are, respectively, the Madelung energy \( E_M \), the electron-ion or band-structure energy \( E_{BS}^{(2)} \) to second order in the electron-ion interaction, the sum of the kinetic, exchange, and correlation energies \( E_{EG} \) of the homogeneous electron gas, the Hartree energy \( E_0 \) (which is the term of first order in the electron-ion interaction), the ionic kinetic energy \( \frac{1}{2} k_B T \) per ion, and the contribution \( -T\mathcal{S} \) from the entropy \( \mathcal{S} \) (all per ion). The individual terms in (6) for a mixture take the following form:

\[
E_M = \frac{1}{2V} \sum_k \sum_{i,j=1}^{2} \sum_{\alpha} \frac{4\pi Z_i Z_j e^2}{k^2} (x_i x_j)^{1/2} [S_{ij}(k) - \delta_{ij}],
\]

\[
E_{BS}^{(2)} = \frac{1}{2V} \sum_k \sum_{i,j=1}^{2} \sum_{\alpha} \sum_{\beta} \frac{k^2}{4\pi\varepsilon^2} \left( \frac{1}{\varepsilon(k)} - 1 \right) \frac{V_p^{(i)}(k) V_p^{(j)}(k)(x_i x_j)^{1/2} S_{ij}(k)}{k^2},
\]

\[
E_{EG} = Z^* \left[ \frac{2.21}{r_s} - \frac{0.916}{r_s} - 0.115 + 0.031 \ln r_s \right] R_y,
\]

\[
E_0 = 2\pi nZ^* e^2 (x_1^2 r_{1H}^2 + x_2^2 r_{2H}^2).
\]

Here \( Z_i \) is the valence of the \( i \)th species, \( x_i \) is the atomic fraction of the \( i \)th species, \( V \) is the total volume of the system, \( S_{ij}(k) \) is the partial ion-ion structure factor, \( \varepsilon(k) \) is the wave-vector-dependent zero-frequency dielectric function of the interacting homogeneous electron gas, \( V_p^{(i)}(k) \) is the bare electron-ion pseudopotential of the \( i \)th species, \( e \) is the electron charge, and \( r_s \) is the electron radius in atomic units, defined by the relation

\[
\frac{V}{NZ^*} = \frac{4\pi}{3} r_s^3,
\]

where \( Z^* = x_1 Z_1 + x_2 Z_2 \) is the average valence and \( N \) is the total number of ions. It is generally convenient to use for the pseudopotential the Ashcroft empty-core form:

\[
V_p^{(i)}(k) = -4\pi Z_i e^2 k^2 \cos(kr_s) / k^2.
\]

With the use of (12), the Hartree term \( E_0 \) takes the form given in Eq. (10); the notation \( r_{1H} \) and \( r_{2H} \) denotes the fact that the core radii \( r_i \) entering into the Hartree term are generally chosen to differ from those used in the band-structure energy \( E_{BS}^{(2)} \). Finally, \( n = N/V \) is the ionic number density. The partial ionic structure factors \( S_{ij}(k) \) are defined in the usual way as

\[
S_{ij}(k) = \frac{1}{(x_i x_j)^{1/2}} \left\{ \sum_{\alpha,\alpha'} e^{ik\cdot(R_{\alpha}^{(i)} - R_{\alpha'}^{(j)})} \right\} / \sqrt{N \delta_{k,0}},
\]

where \( R_{\alpha}^{(i)} \) is the position of the \( \alpha \)th ion of the \( i \)th species, and the angular bracket denotes an average over the appropriate ensemble.

In order to evaluate Eq. (6) at a given density, concentration, and temperature, one requires a method for calculating the partial ionic structure factors and the entropy. Such a method is provided by the well-known Gibbs-Bogolyubov inequality, which may be written in the form

\[
F \leq F_0 + \langle H - H_0 \rangle_0.
\]

Equation (14) states that the free energy \( F \) of a system described by a Hamiltonian \( H \) is bounded by the free energy \( F_0 \) of a reference system with Hamiltonian \( H_0 \), plus the expectation value of the perturbation \( H - H_0 \), evaluated with respect to the correlation functions of the reference system. In the present problem, it is convenient to choose for a reference system a mixture of hard spheres of different diameters. The structure factors of this reference system are available analytically within the Percus-Yevick approximation, while the hard-sphere free energy exists as an analytic fit to the results of computer simulations. With this reference system, therefore, Eq. (14) effectively defines a variational method for calculating the free energy \( F \). For any \( n, x_1, \) and \( T \), one chooses the two variational parameters (the hard-sphere diameters) so as to minimize the right-hand side of the inequality (14), and then takes the resulting minimum upper bound to approximate \( F \).

To complete the prescription for calculating the inputs for the density-functional formalism, one requires a method for approximating the direct correlation functions \( G_{ij}(r) \). These are extremely difficult to estimate in a reliable way, and errors in these probably form the weakest link in the present calculations. We have used the so-called mean-spherical approximation

\[
G_{ij}(r) = \begin{cases} E_{ij}^{HS}(r), & r < (\sigma_i + \sigma_j)/2 \\ -\Phi_{ij}(r)/k_B T, & r > (\sigma_i + \sigma_j)/2 \end{cases}
\]

where \( E_{ij}^{HS}(r) \) are the hard-sphere direct correlation functions appropriate to a mixture of hard spheres of different diameters [these are, like the corresponding \( S_{ij}^{HS}(k) \)'s, available analytically within the Percus-Yevick approxi-
mation], and \( \Phi_{ij}(r) \) is the screened ion-ion pair potential between an ion of species \( i \) and one of species \( j \), as calculated at the same total ionic density \( n \). \( \Phi_{ij}(r) \) is given within pseudopotential theory by the expression

\[
\Phi_{ij}(r) = \frac{1}{(2\pi)^3} \int d^3k \, \Phi_{ij}(k) e^{ik \cdot r},
\]

\[
\Phi_{ij}(k) = \frac{4\pi Z_i Z_j e^2}{k^2} \left[ 1 + \frac{1}{\epsilon(k)} - 1 \right] \frac{V_p^{ij}(k) V_p^{ij}(k)}{Z_i Z_j (4\pi e^2 / k^2)^2}.
\]  

(16)

In the present calculations, the hard-core diameters used in Eq. (15) were obtained from the condition

\[
\Phi_{ii}(\sigma_i) = \frac{3}{2} k_B T,
\]

(17)

which means that \( \sigma_i \) is the distance of closest approach between two like ions, as determined from classical mechanics, if one of the ions is stationary and the other has kinetic energy \( \frac{1}{2} k_B T \). The hard-sphere diameters obtained from Eqs. (17) will differ slightly from those obtained within the variational approximation, but seem the most appropriate ones to use, since there is no particular reason why variational hard-sphere diameters should be the optimum ones from which to calculate correlation functions.

Once the Helmholtz free energy is known as a function of density, alloy concentration, and temperature, the chemical potentials needed for the density-functional formalism can be obtained from the following thermodynamic relations.

If \( N_i \) is the number of ions of type \( i \) in a homogeneous alloy of volume \( V \), then we have

\[
d\mathcal{F} = -\bar{S} \, dT - P dV + \mu_1 dN_1 + \mu_2 dN_2 \\
= -\bar{S} \, dT - P dV + [x\mu_1 + (1-x)\mu_2] dN \\
+ N(\mu_1 - \mu_2) dx,
\]

(18)

where \( \mathcal{F} = nF \) is the total Helmholtz free energy, \( N_1 = xN, N_2 = (1-x)N \), and \( \bar{S} = NS \) is the total entropy (not per ion). From this thermodynamic relation it follows that

\[
x\mu_1 + (1-x)\mu_2 = \frac{\partial \mathcal{F}}{\partial N} \bigg|_{T,V,x},
\]

(19)

\[
\mu_1 - \mu_2 = \frac{1}{N} \frac{\partial \mathcal{F}}{\partial x} \bigg|_{T,V,N}.
\]

(20)

The boundary conditions are

\[
x_0 \mu_1 + (1-x_0) \mu_2 = F(n_1),
\]

(21)

\[
\mu_1 - \mu_2 = \frac{\partial F}{\partial x} \bigg|_{n_1, T},
\]

(22)

where \( n_1 \) is the density of the homogeneous liquid alloy of concentration \( x_0 \), temperature \( T \). Solving these gives

\[
\mu_1 = F(n_1) + (1-x_0) \frac{\partial F}{\partial x} \bigg|_{n_1, T},
\]

(23)

\[
\mu_2 = F(n_1) - x_0 \frac{\partial F}{\partial x} \bigg|_{n_1, T},
\]

(24)

which gives the two chemical potentials \( \mu_1 \) and \( \mu_2 \) needed for execution of the density-functional theory, in terms of the properties of the homogeneous alloy.

III. APPLICATION TO Na\(_x\)K\(_{1-x}\)

In order to test the formalism just described, we have chosen to apply it to the simplest liquid metal alloy, namely, a binary mixture of two alkali metals, Na and K, which are miscible in the liquid state over the entire range of concentration. This system has been selected because it has long been known that the thermodynamic properties of homogeneous liquid alkalies, and their alloys, are quite accurately treated within the formalism just outlined, and because the density-functional theory in the gradient approximation gives rather good results for the surface tension of the pure liquid alkalies. While experimental data is more readily available for the polyvalent alloys at present, the gradient theory has not yet achieved the same results for the pure polyvalent liquid metals.

The calculation of the surface tension of the alloy involves three steps: (i) evaluation of the terms in the free-energy density and the gradient coefficient, (ii) evaluation of the chemical potentials appropriate to the concentration and pressure of interest in the bulk liquid (usually the pressure will be atmospheric pressure—effectively zero pressure in comparison to the energy scale of the other terms in the free energy), and (iii) minimization of the free-energy functional to obtain the surface tension. This last step could, in principle be done exactly by writing out the Euler-Lagrange equation appropriate to the minimization and solving it directly. In practice, this would be a very difficult undertaking, and we have chosen to minimize the surface tension with respect to a surface density profile that depends on one or two parameters only.

To carry out the minimization, we parametrize the interface in terms of \( n(z) \) and \( x(z) \), the position-dependent density, and concentration of component 1. For the density profile, we use the following function:

\[
n(z) = \frac{n_1 + n_0}{2} + \frac{n_1 - n_0}{2} \tanh(z/w),
\]

(25)

where \( n_1 \) is the density of the liquid and \( n_0 \) is that of the coexisting vapor phase and is taken as zero since it is much smaller than \( n_1 \) at the temperatures considered. This hyperbolic tangent density profile has been shown to give very good results for the surface tension of the alkali metals, and may give reasonable results for the overall surface width also. It does not, of course, allow for density oscillations, which D'Evelyn and Rice and Gryko and Rice have suggested may be present in liquid alkalies.

Two concentration profiles have been considered. The simplest is a constant profile, \( x(z) = x_0 \), where \( x_0 \) is the bulk concentration, corresponding to no surface segregation at all. We have also used a hyperbolic tangent concentration profile:
where $x_\ast$ is a variational parameter and $w$ is the same width parameter as in (25). (Allowing a different width parameter $w'$ would be more reasonable, but leads to a computationally more difficult three variational parameters in the surface tension functional.) We note that the hyperbolic tangent concentration profile has the correct asymptotic exponential behavior in both liquid and vapor limits, as predicted by Widom.\textsuperscript{11}

With these parametrized profiles, the expression for the surface tension [Eqs. (2) and (4)] is readily minimized with respect to the two unknown parameters $w$ and $x_\ast$; the results are as follows:

\begin{align}
\tau(x_\ast) & = 2[A(x_\ast)B(x_\ast)]^{1/2}, \\
\omega(x_\ast) & = [B(x_\ast)/A(x_\ast)]^{1/2}, \\
A(x_\ast) & = \int_{-1}^{1} f[n(y), x(y)] - [\mu_1 x(y) + \mu_2 (1 - x(y))] n(y) \, dy, \\
n(y) & = \frac{1}{2} n_\ast (1 + y), \\
x(y) & = \frac{1}{2} (x_0 + x_\ast) + \frac{1}{2} (x_0 - x_\ast) y, \\
B(x_\ast) & = \frac{1}{2} n_\ast^2 [K_{\text{eff}} + \frac{1}{2} (x_0 - x_\ast)^2 K], \\
K & = K_{11}(\bar{n}_1) - 2K_{12}(\bar{n}_1, \bar{n}_2) + K_{22}(\bar{n}_2), \\
K_{\text{eff}} & = K_{11}(\bar{n}_1) x^2 + 2K_{12}(\bar{n}_1, \bar{n}_2) x (1 - x) + K_{22}(\bar{n}_2)(1 - x)^2.
\end{align}

$\bar{n}_1$ and $\bar{n}_2$ are chosen to be $\frac{1}{2} n_\ast x_0$ and $\frac{1}{2} n_\ast (1 - x_0)$.

In applying these results to Na$_x$K$_{1-x}$, we have made the additional assumption that the atomic volume of the alloy is a linear function of concentration ("Vegard's law"). In principle, the actual variation of atomic volume could be computed directly using the present formalism, but previous work on homogeneous liquid alloys has suggested that other quantities of interest (the heat of mixing, for example) are not significantly affected by the assumption that the atomic volumes vary linearly, and so, in the interest of computational convenience, we have assumed the same here.

Table I shows the input parameters for $K$ and Na used in carrying out our calculations. The core radii $r_i$ are taken from Wood and Stroud, and were determined there from fits to resistivity of the pure liquid metal. The core radii $r_{\text{eff}}$ are chosen so as to give the correct zero-pressure density of the pure liquid metal at melting. The only other parameter required is the exchange-correlation function $G(k)$ used in calculating the dielectric function; we have followed Wood and Stroud in using the Hubbard-Geldard-Vosko interpolation scheme for this function, as described in Ref. 9. Note that the core radii and densities are the only input parameters to the problem; everything else (free energy of the bulk liquid, surface tension of the pure constituents, and variation of surface tension and surface profile of the liquid alloy) is computed from first principles.

The surface tension of liquid Na$_x$K$_{1-x}$ is plotted in Fig. 1 as a function of concentration for a number of different temperatures. In all cases, we have found that the "surface concentration parameter" $x_\ast = 0$, giving maximum surface segregation. In order to compare with the effect of no surface segregation, we show also in Fig. 1 the result of using a constant-concentration profile ($x_\ast = x_0$). As is clear, the curves with a hyperbolic tangent concentration profile show the expected rapid drop of $\tau$ near $x = 1$ (small concentration of the low-surface-tension K impurities), while the constant-concentration-profile curve does not.

Figure 1 also makes clear the effect of temperature. The influence of surface segregation is more pronounced at low temperatures than at high temperatures (it would eventually become very small at sufficiently high temperatures). This behavior is expected since at the lower temperature the contribution to $\tau$ is dominated by surface energy, which will be smaller if the surface is more populated by the smaller-$\tau$ component. At higher temperatures, the effects of surface entropy would be expected to decrease the segregation.

To show the segregation effect more directly, we plot the density profiles of each of the components in Figs. 2 through 5. When $x_0 > 0.5$, the density of potassium, $n_K(x)$, develops a maximum; this maximum is most distinct at $x = 0.02$, indicating very strong segregation of K to the surface at this concentration.

| TABLE I. Input parameters used in the calculation. The columns represent the density at melting temperature ($T_m = 371$ K) of Na, empty core radius $r_{\text{eff}}$ used to fit the zero-pressure density. |
|-----------------|-----------------|-----------------|
| $10^3 n_a a_0^2$ | $r_i / a_0$ | $r_{\text{eff}} / r_i$ |
| Na              | 3.598          | 1.69            | 1.08            |
| K               | 1.861          | 2.226           | 1.12            |
FIG. 1. Calculated surface tension $\tau$ (dots) of $\text{Na}_x\text{K}_{1-x}$ as a function of the concentration $x$. The curve labeled as constant concentration shows the results of assuming concentration constant through the surface. All the other curves are results of using hyperbolic tangent concentration profile at different temperatures. Also shown are the experimental surface tensions of pure K and Na.

FIG. 2. Density profile of the compounds of $\text{Na}_x\text{K}_{1-x}$ at $T=371$ K. The vertical axis is normalized to the bulk density. The horizontal axis shows the distance into the bulk liquid. This graph is plotted for $x_{\text{Na}}=0.2$.

FIG. 3. Same as Fig. 2 but for $x_{\text{Na}}=0.6$.

FIG. 4. Same as Fig. 2 but for $x_{\text{Na}}=0.8$.
FIG. 5. Same as Fig. 2 but for $x_{Na} = 0.98$.

IV. DISCUSSION

While there are no experimental data available for the alloy system considered in this paper, the experimental surface tension has been carefully measured as a function of concentration for the polyvalent liquid alloy system $Sn_xGa_{1-x}$, which is miscible over the entire concentration range.$^{13}$ This alloy system shows (i) an apparent minimum in surface tension as a function of concentration, possibly associated with an approaching phase separation, and (ii) a dramatic drop in surface tension near $x = 0$, i.e., a small concentration of the low-surface-

tension impurity. The latter effect is in agreement with present predictions. Figure 6 shows the calculated surface concentration of $Sn$, as deduced from the experimental surface tension and a monolayer phenomenological surface model as discussed below, plotted as a function of the bulk concentration. This surface concentration is in agreement with the value of $x$ deduced from Auger electron spectroscopy of the surface.$^{13}$

The present dramatic segregation effect at $x \sim 1$ in $Na_xK_{1-x}$ can be qualitatively understood, just as can the results for $Ga_xSn_{1-x}$, by the so-called surface monolayer model. This model assumes that the alloy consists of a bulk with concentration $x$, and a single monolayer of surface with concentration $x'$. Simple thermodynamic relations then lead to the following result as shown in Ref. 14:

$$x'_2 = \frac{x_2 + x_A\Gamma_1^{(1)}}{1 + (A_2 - A_1)x_1\Gamma_2^{(1)}},$$

(35)

FIG. 6. Surface concentration $x'$ of $Sn$ as a function of bulk concentration $x$ at $T = 623$ K for liquid metal alloy $Ga_{1-x}Sn_x$. This result is taken from Ref. 13.

FIG. 7. Calculated surface concentration $x'_K$ (dots) of $K$ as a function of bulk concentration $x_K$ at $T = 371$ and 600 K for liquid metal alloy $Na_{1-x}K_x$. 

where $A_1$ and $A_2$ are atomic areas, i.e., areas per atom of types 1 and 2. The relative adsorption $\Gamma_2^{(1)}$ of component 2 with respect to component 1 at the surface is given by the Gibbs equation

$$\Gamma_2^{(1)} = \frac{1}{k_B T} \left[ \frac{\partial \tau}{\partial \ln a_2} \right] \bigg|_{a_1} ^{a_2},$$

where $a_1$ is the thermodynamic activity defined through

$$\mu_i = \mu_i^0 + k_B T \ln a_i$$

and $\mu_i^0$ is the chemical potential of pure component $i$.

In the dilute limit ($x_2 \rightarrow 0$), $a_2 = x_2$ (Henry's law), and Eq. (35) becomes

$$x = \left[ x - \frac{x(1-x)A_1}{k_B T} \frac{\partial \tau}{\partial x} \right] \times \left[ 1 - \frac{x(1-x)(A_1 - A_2)}{k_B T} \left( \frac{\partial \tau}{\partial x} \right) \right]^{-1}.$$  

With our calculated results for surface tension $\tau$ as a function of $x$ in Fig. 1 and approximation of $A_2 = n_i^{-2/3}$, we can compute $x^\sigma$ as a function of $x$ for Na$_x$K$_{1-x}$. The results are shown in Fig. 7. The behavior displayed in Fig. 7 is similar to the experimental results of Fig. 6, although the former is expected to be good for the dilute case only. The effect of temperature on surface segregation is clearly demonstrated here; for $x_K = 0.05$, $x_K^\sigma = 0.4$ at $T = 371$ K, whereas $x_K^\sigma = 0.3$ at $T = 600$ K.

Finally we note that the segregation effect discussed in the present paper can also be studied by constructing a lattice-gas model for the liquid-vapor interface of an alloy. Work along this line is in progress.

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