ture susceptibility. The next step should be the treatment of a system in which the confining potential is represented by a polynomial of higher order in the coordinate variables. By the inclusion of a sufficient number of terms in the series (2.2) any potential single valued at the surface can be well approximated. In this event a collective restriction must be placed on the magnitude of the numerical coefficients to satisfy the requirements of perturbation theory. Unfortunately the accomplishment of this objective is hindered by the circumstance that the higher order matrix elements encountered lead to the introduction of factors of progressively higher power in temperature, making it very difficult to demonstrate explicitly the cancellation (if indeed it takes place) of all but those terms involving only inverse powers of temperature, such as appear in Eqs. (4.10) and (4.14). By a procedure similar to that used here to treat the quartic potential, the temperature dependence of all corrections to the susceptibility resulting

from an assumed confining potential of the form $V_0(b_4 y^4 + b_6 y^6)$ was verified after some effort. Although it seems highly probable that all terms in the potential (2.2) would lead to a similar temperature variation for $\chi$, there appears to be no practicable way by which this can be conclusively demonstrated using the present analytical approach.

It is interesting to point out that an appropriately scaled potential having the functional form $y^n$ approaches that of a one-dimensional square well as $n$ becomes large; this is possibly significant in light of the fact that the three-dimensional square-well potential is known to lead to a susceptibility having exactly the Landau form with corrections involving only inverse powers of temperature. This circumstance lends some support to the conjecture that any potential single valued at the surface, or equivalently one expressible as a power series in the spatial coordinates, would have exactly the Landau susceptibility at high temperature.

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[11]It is interesting to note that under either the condition $\Omega \gg \omega$ or $\Omega \ll \omega$, the right-hand side of the inequality (3.9) reduces to the same quantity $V_0 b_4 (k T)^2/m^2\Omega^4$, except for a numerical factor of order unity.
[12]The inequality $\omega \gg \Omega$ can also be interpreted to imply a

narrow system in the $y$ direction when compared with the electron's radius of gyration.
[13]The inequalities $\omega \ll \Omega$ and $\beta \hbar \Omega \ll 1$ together imply $\hbar \omega \ll k T$, the condition that ensures that oscillatory phenomena relating to the de Haas–van Alphen effect are small.
[14]For a system obeying classical statistics, which has been assumed here, the conclusions correctly apply only in the high-temperature limit where $k T \gg \hbar \Omega$. However, for real metals, classical statistics are not sufficient and Fermi–Dirac statistics must be used. The low-temperature limit $\eta \gg kT \approx \hbar \Omega$ is then appropriate with the Fermi energy $\eta$ essentially replacing $k T$ in the corresponding conditions and results.
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# Theory of Phase Separation in Liquid-Metal Alloys: Li$_x$Na$_{1-x}$[†]

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The phase separation curves of liquid-metal alloys may be obtained by a variational method which involves no free parameters. The scheme is applied to Li$_x$Na$_{1-x}$ and yields results in good qualitative agreement with experiment.

## I. INTRODUCTION

This is the last in a group of three papers on the subject of phase transformations in liquid and solid metals and alloys. Previous papers have dealt

with the origin of the Hume–Rothery rules for the crystal structures of binary alloys,[1] and with the theory of melting of simple metals.[2] The present paper extends the procedures used in these calculations to apply to a second-order phase transition,

namely, the miscibility gap which is observed in a number of binary liquid metallic alloys. Such a study is of particular relevance at the moment because of the considerable recent experimental interest in fluctuations near the critical point of metallic systems exhibiting a miscibility gap.[3-6] Although the present work deals directly only with the static properties of such systems (i. e. , the phase-separation curve itself), it forms a starting point for an investigation of fluctuation effects from a mean-field point of view. It is hoped in a future paper to deal with fluctuation effects in this manner.

The basis of the calculation is a variational principle which makes it possible to obtain the alloy-free energy, and hence the phase-separation curve, without any free parameters whatsoever. Such a procedure has previously been shown to give good results for the melting curve of Na.[2] When applied to liquid $Li_xNa_{1-x}$, the approach yields a curve in qualitative agreement with experiment. The present work is believed to represent the first calculation of the phase-separation curve in a mixture of liquid metals.[7]

We turn now to a detailed discussion of the calculation. Section II describes the variational method for finding the free energy of any binary liquid metallic alloy. The application to $Li_xNa_{1-x}$ is presented in Sec. III.

## II. FREE ENERGY

The phase-separation curve in a binary liquid mixture $A_xB_{1-x}$ may be calculated at zero pressure from knowledge of Helmholtz free energy per ion, $F$, as a function of concentration and temperature. The calculation requires a well-known graphical procedure illustrated schematically in Fig. 1. For a given temperature $T < T_c$, there is a concentration regime in which the free-energy isotherm is concave downward, so that a straight line may be drawn tangent to the curve at two points. The solubility limits $x_A(T)$ and $x_B(T)$ are the abscissas of the two points of tangency. As $T$ is increased, $x_A$ and $x_B$ move closer together, until at $T = T_c$ they coincide at $x_c$. For $T > T_c$, the isotherms are concave upward at all $x$, the common tangent construction is impossible, and the mixture is stable against separation at any concentration.

In a liquid-metal alloy, $F(x, T)$ can be approximated as

$$F(x, T) \sim E_{kin}^{elec} + E_{xc}^{elec} + E_0 + E_{kin}^{ion} + E_M + E_{BS} - TS . \quad (1)$$

$E_{kin}^{elec}$ and $E_{xc}^{elec}$ are, respectively, the kinetic and exchange-correlation energy per ion of the electron gas, given in rydbergs by

$$E_{kin}^{elec} = (2.21/r_s^2) Z_{eff}, \quad (2)$$

$$E_{xc}^{elec} = (-0.916/r_s - 0.115 + 0.031 \ln r_s) Z_{eff},$$
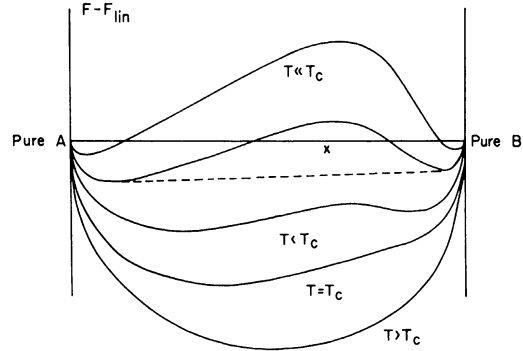


FIG. 1. Schematic of free-energy isotherms in a liquid-metal alloy $A_xB_{1-x}$ exhibiting a miscibility gap. $F - F_{lin}$ is the deviation of the free energy per ion, $F$, from a linear interpolation of the free energies of the constituents. The dashed line is drawn tangent to the isotherm at two concentrations, which represent the solubility limits of the alloy at the corresponding temperature.

where $r_s$ is the electron radius, defined in terms of the ionic density $N$ and effective valence $Z_{eff}$ $= xZ_A + (1 - x) Z_B$ by $\frac{4}{3} \pi r_s^3 = (NZ_{eff})^{-1}$. $E_0$ (the so-called Hartree energy) is equal to the sum of the long-wavelength components of the electron-electron, ion-ion, and electron-ion interactions (each of which is separately divergent):

$$E_0 = [xZ_A \alpha_A + (1 - x) Z_B \alpha_B] N Z_{eff}, \quad (3)$$

where $\alpha_A$ and $\alpha_B$ are constants related to the long-wavelength behavior of the electron-ion pseudopotential. $E_{kin} = \frac{3}{2} k_B T$ is the ionic kinetic energy per ion. $E_M$, the Madelung energy per ion, is

$$E_M = \frac{1}{2} \sum_{k \neq 0} \frac{8\pi}{k^2} \{ xZ_A^2 (S_{AA}(k) - 1) + 2[x(1 - x)]^{1/2}$$
$$\times Z_A Z_B S_{AB}(k) + (1 - x) Z_B^2 [S_{BB}(k) - 1] \}, \quad (4)$$

$S_{AA}$, $S_{AB}$, and $S_{BB}$ being the partial ionic structure factors appropriate to the alloy. The band-structure energy per ion, $E_{BS}$, can also be expressed in terms of the structure factors provided that the pseudopotentials $V_k^A$ and $V_k^B$ are weak. The result, valid to second order in the pseudopotentials, is

$$E_{BS} = \frac{1}{2} \sum_{k \neq 0} \frac{k^2}{8\pi} \{ x| V_k^A |^2 S_{AA}(k) + 2[x(1 - x)]^{1/2}$$
$$\times V_k^A V_k^B S_{AB}(k) + (1 - x)| V_k^B |^2 S_{BB}(k) \} \left( \frac{1}{\epsilon_k} - 1 \right), \quad (5)$$

where $\epsilon_k$ is the dielectric function of the electron gas. The last term in (1) represents the contribution of the entropy $S$ to the free energy.

Expression (1) can readily be evaluated if the structure factors and entropy of the liquid alloy are

chosen to correspond to a mixture of hard spheres of different diameters $D_A$ and $D_B$. Both structure factors[8] and entropy[9] are available analytically for such a system in the Percus–Yevick[10] approximation.

$D_A$ and $D_B$ may be unambiguously determined with the help of the variational principle mentioned earlier. The basis of the scheme is an inequality derived from thermodynamic perturbation theory, which for the present application may be written[11]

$$F \leq F_0 + \langle V \rangle_0 . \tag{6}$$

Here $F_0$ is the free energy of the reference mixture of hard spheres, and $\langle V \rangle_0$ represents the ion-ion interaction energy, calculated using the true pair potentials and hard-sphere structure factors. In (1), the role of $\langle V \rangle_0$ is played by $E_M + E_{BS}$, which behaves like a sum of pairwise interactions between the ions, while the remaining terms correspond to $F_0$. Note that the pairwise ion-ion interaction energy is zero in the hard-sphere reference system. Thus expression (1), calculated with hard-sphere structure factors and entropy, is in reality an *upper bound* to the free energy for any choice of $D_A$ and $D_B$. The variational prescription for calculating $F(x, T)$ is therefore (a) for each $x$ and $T$, minimize expression (1) with respect to $D_A$ and $D_B$ [thereby obtaining effective concentration- and temperature-dependent hard-sphere diameters $D_A(x, T)$ and $D_B(x, T)$], and (b) let the resulting minimum upper bound approximate $F$.

The accuracy of this approach presumably depends on the degree to which the liquid mixture resembles the reference mixture of hard spheres. For a system in which the liquid structure factors deviate greatly from those of a hard-sphere system, we may expect that the variational upper bound will be much greater than the true free energy.

### III. APPLICATION TO $Li_x Na_{1-x}$

A mixture of liquid Li and Na represents a particularly appropriate system for application of the present variational scheme. The experimental structure factors of both pure liquids are reasonably well fitted[12] by those of hard spheres in the Percus–Yevick approximation; it is therefore plausible that those of the mixture will be well repreted by the structure factors of a mixture of hard spheres of different diameters. Moreover, of all metallic systems exhibiting miscibility gaps, the weak-pseudopotential approximation best applies to $Li_x Na_{1-x}$. The hard-sphere model is less successful in describing the structure factors of polyvalent metals.[12] Moreover, there is some doubt that second-order perturbation theory is sufficient for their alloys.

Application of the variational approach to liquid

$Li_x Na_{1-x}$ is straightforward. In the present work, the pseudopotentials have been chosen to be of the local and energy-independent Ashcroft form[13]:

$$V_k^{Li, Na} = -(8\pi/k^2)\cos k r_c^{Li, Na} . \tag{7}$$

$r_c^{Na}$ has been taken to be 1.67 a.u., which fits Fermi-surface and transport data. Such measurements do not uniquely determine $r_c^{Li}$, which has therefore been chosen in such a way that the corresponding variationally determined hard-sphere packing fraction $\eta = \frac{1}{6}\pi D_{Li}^3 N$ equals 0.45 at melting, which best fits the observed liquid structure factors. $\alpha_{Li}$ and $\alpha_{Na}$ have been chosen so that $F(x, T)$ satisfies the zero-pressure conditions $dF/dr_s = 0$ at the observed equilibrium volumes of *liquid* Li and Na at melting. For the dielectric function $\epsilon_k$, the Hubbard[14] form, suitably adjusted to satisfy the compressibility sum rule, has been used.[15]

The calculated phase-separation curve for $Li_x Na_{1-x}$ is compared with experiment in Fig. 2. The experimental points represent the work of Salmon and Ahmann,[16] with the exception of the critical point, measured by Schürmann and Parks.[3] The absence of a theoretical point at $T_c$ is a result of numerical difficulties—the free-energy curve is so flat at such temperatures that it becomes very difficult to determine whether a common tangent construction is possible. Nevertheless, the theoretical curve reproduces the observed asymmetry, and in particular approximately matches the measured $x_c$ of about 70-at.% Li. $T_c$ is,
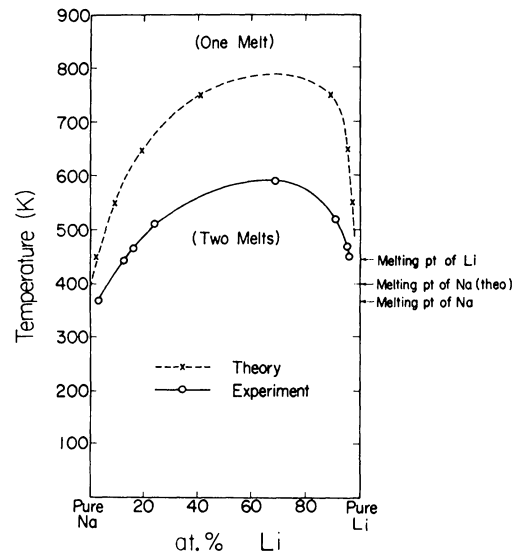


FIG. 2. Phase-separation curve in liquid $Li_x Na_{1-x}$. The experimental curve is based on Salmon and Ahmann, Ref. 16, and Schürmann and Parks, Ref. 3. The theoretical melting point of Na is from Stroud and Ashcroft, Ref. 2.

however, overestimated by about a third. This discrepancy can be blamed on the extreme sensitivity of the theoretical curve to small errors in the free-energy calculation—an error of only about 0.4 mRy/ion (less than 0.1% of the free energy of the mixture) could lead to the observed deviation. We note, however, that the overestimate of $T_c$ may also be an inevitable consequence of using a mean-field theory, in which $|x_A - x_B| \propto (T_c - T)^{1/2}$ near $T_c$, rather than the flatter experimental behavior $|x_A - x_B| \propto (T_c - |T)^{0.3-0.35}$.

Despite sensitivity of the calculation, the good qualitative results illustrated in Fig. 2 cannot be considered merely fortuitous. The melting curve of Na, obtained in Ref. 2 by a method in which the liquid state is treated exactly as in the present calculation, also agrees well with experiment; the computed zero-pressure melting point, shown in Fig. 2, deviates from observation by only 5%. Furthermore, the method seems capable of predicting the behavior of liquid mixtures other than $Li_xNa_{1-x}$. For liquid $Na_{0.5}K_{0.5}$ at 400 °K, it yields a free energy of mixing $\Delta F = \frac{1}{2}(F_{Na} + F_K) - F_{Na_{0.5}K_{0.5}}$ = 1.5 mRy/ion. Since a positive $\Delta F$ is a necessary condition for the alloy to form, this result is consistent with the fact that at $T = 400$ °K, liquid $Na_xK_{1-x}$ is stable at any concentration.

The various contributions to $\Delta F$ in liquid $Li_{0.5}Na_{0.5}$ are listed in Table I for $T = 850$ °K. A term with a positive contribution to $\Delta F$ favors the mixing of the two metals. Note that a major contribution comes from the terms $E_{kin}^{elec}$, $E_{xc}^{elec}$, and $E_0$, which do not depend on the liquid structure. Among these terms, $E_0$ in particular is hard to calculate with great accuracy. Until one can be confident of such accuracy, the phase-separation curve is unlikely to be calculable with quantitative

TABLE I. Contributions to the free energy of mixing $\Delta F = \frac{1}{2}(F_{Li} + F_{Na}) - F_{Li_{0.5}Na_{0.5}}$ at $T = 850$ °K. Row by row, the contributions are due to the electronic kinetic energy $E_{kin}^{elec}$, the electronic exchange-correlation energy $E_{xc}^{elec}$, the Hartree energy $E_0$, the entropy term $- TS$, the Madelung energy $E_M$, and the band-structure energy $E_{BS}$. The ionic kinetic energy makes no contribution.

| Free-energy term | Contribution to $\Delta F$ (mRy/ion) |
|---|---|
| $E_{kin}^{elec}$ | +8.3 |
| $E_{xc}^{elec}$ | −5.5 |
| $E_0$ | +1.3 |
| $- TS$ | +4.7 |
| $E_M$ | −12.7 |
| $E_{BS}$ | +4.8 |
| Total | +0.9 |

precision, no matter how sophisticated the treatment of statistical correlations in the liquid. Table I also shows that, in contrast to the situation which prevails in structural phase transitions in solid alloys,[1] the electron-ion energy $E_{BS}$ does not play a dominant role in the phase-separation curve; its contribution is only one of several major terms in $\Delta F$.

## ACKNOWLEDGMENTS

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