tured 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 \( V_0 (b_x y^4 + b_y y^6) \) 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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1L. Landau, Z. Phys. 64, 629 (1930).
11It 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 \( V_b \Omega k T / m \Omega \), except for a numerical factor of order unity.
12The 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.
13The inequalities \( \omega \ll \Omega \) and \( \beta \Omega \ll 1 \) together imply \( \Omega \omega \ll k T \), the condition that ensures that oscillatory phenomena relating to the de Haas–van Alphen effect are small.
14For a system obeying classical statistics, which has been assumed here, the conclusions correctly apply only in the high-temperature limit where \( k T \gg \Omega \). However, for real metals, classical statistics are not sufficient and Fermi-Dirac statistics must be used. The low-temperature limit \( \eta \gg kT \approx \Omega \) 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_{1-x}Na_{x}

D. Stroud
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850
Department of Physics, Ohio State University, Columbus, Ohio 43210

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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_{1-x}Na_{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, and with the theory of melting of simple metals. The present paper extends the procedures used in these calculations to apply to a second-order phase transition,
nanneth, the miscibility gap which is observed in a
dumber of binary liquid metallic alloys. Such a
study is of particular relevance at the moment be-
cause of the considerable recent experimental in-
terest in fluctuations near the critical point of met-
alic systems exhibiting a miscibility gap. 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 man-
ner.

The basis of the calculation is a variational prin-
ciple 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._4 When applied
to liquid Li_2Na, the approach yields a curve in
qualitative agreement with experiment. The pres-
ent work is believed to represent the first calcu-
lation of the phase-separation curve in a mixture of
liquid metals._7

We turn now to a detailed discussion of the cal-
culation. Section II describes the variational method
for finding the free energy of any binary liquid me-
tallic alloy. The application to Li_2Na is pre-
sented in Sec. III.

II. FREE ENERGY

The phase-separation curve in a binary liquid
mixture A_B 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
region in which the free-energy isotherm is con-
cave downward, so that a straight line may be
drawn tangent to the curve at two points. The solu-
bility 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 con-
cave upward at all x, the common tangent con-
struction is impossible, and the mixture is stable
against separation at any concentration.

In a liquid-metal alloy, F(x, T) can be approxi-
mated as

$$F(x, T) \sim E_{\text{flec}} + E_{\text{exc}} + E_0 + E_{\text{is1s}} + E_{\text{eff}} - TS.$$  

(1)

$$E_{\text{flec}}$$ and $$E_{\text{exc}}$$ are, respectively, the kinetic and
exchange-correlation energy per ion of the electron
gas, given in rydbergs by

$$E_{\text{flec}} = (2.21/r_x^2) Z_{\text{eff}},$$

$$E_{\text{exc}} = (-0.916/r_x - 0.115 + 0.031 \ln r_x) Z_{\text{eff}},$$  

(2)

where r_x is the electron radius, defined in terms
of the ionic density N and effective valence Z_{\text{eff}}
$$x Z_A + (1 - x) Z_B$$ by
$$\frac{1}{2} \pi r_x^2 = (NZ_{\text{eff}})^{\frac{1}{3}}.$$  

E_0 (the so-called Hartree energy) is equal to the sum of
the long-wavelength components of the electron-elec-
tron, ion-ion, and electron-ion interactions (each
of which is separately divergent):

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

(3)

where $$\alpha_A$$ and $$\alpha_B$$ are constants related to the lon-
g-wavelength behavior of the electron-ion pseudopo-
tential. E_{\text{is1s}} = \frac{1}{2} k_0 T$$ is the ionic kinetic energy per
ion. E_{\text{eff}}, the Madelung energy per ion, is

$$E_{\text{eff}} = \sum_{k \neq 0} \frac{8 \pi}{k^2} \left( x Z_A (S_{AA}(k) - 1) + 2 [x(1-x)]^{1/2} \right)$$

$$\times Z_A Z_B S_{AB}(k) + (1 - x) Z_B^2 [S_{BB}(k) - 1],$$  

(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_{\text{bs}}, can also be expressed in terms of the structure factors provided that the pseudopotentials $$V^A$$ and $$V^B$$ are weak. The result, valid to second order in the pseudopotentials, is

$$E_{\text{bs}} = \sum_{k \neq 0} \frac{k^2}{8 \pi} \left( 4 Z_A^4 S_{AA}(k) + 4 [x(1-x)]^{1/2} \right)$$

$$\times V^A V^B S_{AB}(k) + (1 - x) \left[ V^B \frac{k^2}{8} S_{BB}(k) \right] \frac{1}{6_k} - 1,$$  

(5)

where $$\epsilon_k$$ is the dielectric function of the electron
gas. The last term in (1) represents the contribu-
tion 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 and entropy are available analytically for such a system in the Percus–Yevick 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

$$F \leq F_0 + \langle V \rangle_0.$$  \hspace{1cm} (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 $E_Y + E_{NS}$, 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$_2$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 to those of hard spheres in the Percus–Yevick approximation; it is therefore plausible that those of the mixture will be well represented 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$_2$Na$_{1-x}$. The hard-sphere model is less successful in describing the structure factors of polyvalent metals. Moreover, there is some doubt that second-order perturbation theory is sufficient for their alloys.

Application of the variational approach to liquid Li$_2$Na$_{1-x}$ is straightforward. In the present work, the pseudopotentials have been chosen to be of the local and energy-independent Ashcroft form:

$$\gamma_{Li}^{Li,Na} = -(8\pi/k^3)\cos k\gamma_{Li}^{Li,Na}.$$ \hspace{1cm} (7)

$\gamma_{Li}^{Na}$ has been taken to be 1.67 a.u., which fits Fermi-surface and transport data. Such measurements do not uniquely determine $\gamma_{Li}^{Li,Na}$; which has therefore been chosen in such a way that the corresponding variationally determined hard-sphere packing fraction $\eta = \frac{1}{2} \pi D^3_A N$ equals 0.45 at melting, which best fits the observed liquid structure factors. $\zeta_{Li}$ and $\zeta_{Na}$ have been chosen so that $F(x, T)$ satisfies the zero-pressure conditions $dF/dx = 0$ at the observed equilibrium volumes of liquid Li and Na at melting. For the dielectric function $\varepsilon_{Li}$, the Hubbard form, suitably adjusted to satisfy the compressibility sum rule, has been used.

The calculated phase-separation curve for Li$_2$Na$_{1-x}$ is compared with experiment in Fig. 2. The experimental points represent the work of Salmon and Ahmann, with the exception of the critical point, measured by Schmüser and Parks. 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$_2$Na$_{1-x}$. The experimental curve is based on Salmon and Ahmann, Ref. 15, and Schmüser and Parks, Ref. 3. The theoretical melting point of Na is from Stroud and Ashcroft, Ref. 2.](image)
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 $T_e$ may also be an inevitable consequence of using a mean-field theory, in which $|x_e - x_0| \approx (T_e - T)^{1/2}$ near $T_e$, rather than the flatter experimental behavior $|x_e - x_0| \approx (T_e - T)^{0.3-0.35}$.

Despite sensitivity of the calculation, the good qualitative results illustrated in Fig. 2 cannot be considered merely fortuitous. The melting curve of Na$_2$ is obtained in Fig. 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$_x$Na$_{1-x}$. 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$_{0.5}$K$_{0.5}$ 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 $E_{\text{elas}}^{\text{elex}}$, $E_{\text{xc}}^{\text{elex}}$, and $E_{\text{el}}$, which do not depend on the liquid structure. Among these terms, $E_{\text{el}}$ 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 precision, no matter how sophisticated the treatment of statistical correlations in the liquid. Table I also shows that, in contrast to the situation which prevals in structural phase transitions in solid alloys, the electron-ion energy $E_{\text{BS}}$ does not play a dominant role in the phase-separation curve; its contribution is only one of several major terms in $\Delta F$.

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*Present address.


15The form is given explicitly in Ref. 2.