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Theory of Phase Separation in Liquid Metal Alloys: $\text{Li}_x\text{Na}_{1-x}$ *

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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 $\text{Li}_x\text{Na}_{1-x}$ 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 alloys¹, and with the theory of melting of simple metals². 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 $\text{Li}_x\text{Na}_{1-x}$, 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 $\text{Li}_x\text{Na}_{1-x}$ is presented in Section III.

II. Free Energy

The phase separation curve in a binary liquid mixture $A_x B_{1-x}$ 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

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

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

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

$$E_{\text{xc}}^{\text{elec}} = (-0.916/r_s - 0.115 + 0.031 \ln r_s) Z_{\text{eff}} \quad (2)$$

where r_s is the electron radius, defined in terms of the ionic density N and effective valence $Z_{\text{eff}} = xZ_A + (1 - x)Z_B$ by $(4\pi/3)r_s^3 = (NZ_{\text{eff}})^{-1}$. 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):

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

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

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

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

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

where ϵ_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 factors⁸ and entropy⁹ are available analytically for such a system in the Percus-Yevick¹⁰ 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 written¹¹

$$F \leq F_0 + \langle V \rangle_0 \quad (6)$$

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 . 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 $\text{Li}_x\text{Na}_{1-x}$

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 fitted¹² by 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 $\text{Li}_x\text{Na}_{1-x}$. 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 $\text{Li}_x\text{Na}_{1-x}$ is straightforward. In the present work, the pseudo-potentials have been chosen to be of the local and energy-independent Ashcroft form:¹³

$$v_k^{\text{Li,Na}} = - \frac{8\pi}{k^2} \cos kr_c^{\text{Li,Na}} \quad (7)$$

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 $\eta = \frac{\pi}{6} D_{\text{Li}}^3 N$ equals 0.45 at melting, which best fits the observed liquid structure factors. α_{Li} and α_{Na} have been chosen so that $F(x,T)$ satisfies the zero-pressure conditions $dF/dr_g = 0$ at the observed equilibrium volumes of liquid Li and Na at melting. For the dielectric function ϵ_k , the Hubbard¹⁴ form, suitably adjusted to satisfy the compressibility sum rule, has been used.¹⁵

The calculated phase separation curve for $\text{Li}_x\text{Na}_{1-x}$ is compared with experiment in Fig. 1. 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% Li. T_c is, 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 millirydbergs/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 $|x_A - x_B| \propto (T_c - T)^{\frac{1}{2}}$ 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 $\text{Li}_x\text{Na}_{1-x}$. For liquid $\text{Na}_{0.5}\text{K}_{0.5}$ at 400°K , it yields a free energy of mixing $\Delta F = \frac{1}{2}(F_{\text{Na}} + F_{\text{K}}) - F_{\text{Na}_{0.5}\text{K}_{0.5}} = 1.5$ millirydbergs/ion. Since a positive ΔF is a necessary condition for the alloy to form, this result is consistent with the fact that at $T = 400^\circ\text{K}$ liquid $\text{Na}_x\text{K}_{1-x}$ is stable at any concentration.

The various contributions to ΔF in liquid $\text{Li}_{0.5}\text{Na}_{0.5}$ are listed in Table I for $T = 850^\circ\text{K}$. A term with a positive contribution to ΔF favors the mixing of the two metals. Note that a major contribution comes from the terms $E_{\text{kin}}^{\text{elec}}$, $E_{\text{xc}}^{\text{elec}}$, and E_0 , which 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 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 ΔF .

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Figure Captions

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.

Fig. 2: Phase separation curve in liquid Li_xNa_{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.

TABLE I

<u>Free Energy Term</u>	<u>Contribution to ΔF</u>
E_K^{elec}	+8.3 millirydbergs/ion
E_{xc}^{elec}	-5.5
E_o	+1.3
$-T\mathcal{S}$	+4.7
E_M	-12.7
E_{BS}	+4.8
Total	+0.9 millirydbergs/ion

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

Figure 1

Figure 2