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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

STRUCTURE AND FORCES IN LIQUIDS AND LIQUID MIXTURES

Summary of Lecture VI

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Summary of main results to date on mixtures

1. $S_{cc}(0) = N\langle(\Delta c)^2\rangle = N k_B T \Big/ \left(\frac{\partial^2 G}{\partial c^2}\right)_{T,p,N}$

2. $S_{NN}(0) = (N/\Omega) k_B T K_T + \delta^2 S_{cc}(0)$

   (K_T: alloy compressibility; δ: size difference factor)

3. $S_{Nc}(0) = -\delta S_{cc}(0)$.

4. $\frac{1}{(2\pi)^3}\int [S_{NN}(q) - 1]\, dq = -\frac{N}{\Omega}$

5. $\int [S_{cc}(q) - c(1-c)]\, dq = 0$

6. $\int S_{Nc}(q)\, dq = 0$.

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7. Conformal soln $S_{cc}(0)$ is

$$S_{cc}(0) = \frac{c(1-c)}{1 - 2\frac{w}{RT}\cdot c(1-c)}.$$

Structure factors at $k = 0$ in terms of $N\langle(\Delta c)^2\rangle \equiv S_{cc} = N k_B T \Big/ \frac{\partial^2 G}{\partial c^2}\Big|_{T,p,N}$,

size and compressibility

Define $a_{\alpha\beta}(k) = 1 + 4\pi\rho \int_0^\infty [g_{\alpha\beta}(r) - 1] \frac{\sin kr}{kr} r^2 dr$

(ρ: Total no of atoms N)

Then for arbitrary concentration, Ω and $k = 0$, Bhatia and Thornton (1970) show:

$$a_{11} = \Theta + \left[\frac{1}{(1-c)^2} - \frac{2\delta}{1-c} + \delta^2\right] S_{cc} - \frac{c}{1-c}$$

$$a_{22} = \Theta + \left[\frac{1}{c^2} + \frac{2\delta}{c} + \delta^2\right] S_{cc} - \frac{1-c}{c}$$

$$a_{12} = \Theta + \left[\delta^2 - \frac{(2c-1)\delta}{c(1-c)} - \frac{1}{c(1-c)}\right] S_{cc} + 1$$

$\Theta = \rho k_B T K_T$ — compressibility of alloy

$\delta = -\frac{1}{\Omega}\left(\frac{\partial \Omega}{\partial c}\right)_{T,p,N}$

We'll give the argument later. First use in connection with model of REGULAR SOLUTION.

As further application of conformal (regular) solution theory for liquid metal alloys, we shall sketch calculation of phase diagram of Na-K.

Liquidus curve of an ideal soln. has been known to have approx. form

$$\ln(1-c_2) = (L_{10}/R)\left[T_1^{-1} - T^{-1}\right],$$

c_2 being concentration of element 2, and L_{10} the latent heat at freezing temperature T_1 of pure liquid 1.

Thermodynamic eqns along liquidus

In terms of chemical potentials (subscript zero referring to a pure substance and superscript S denoting solid)

$$\mu_{10}^{S}(T) = \mu_1(T, c_2)$$

with the differential form

$$\frac{\Delta T}{\Delta c_2} = -\left(\frac{\partial \mu_1}{\partial c_2}\right)_{p,T} \Big/ \left[\left(\frac{\partial \mu_1}{\partial T}\right)_{c_2,p} - \left(\frac{\partial \mu_{10}^{S}(T)}{\partial T}\right)_p\right]$$

$$= \left(\frac{\partial \mu_1}{\partial c_2}\right)_{p,T} / (L/T) = -c_2\left(\frac{\partial^2 G}{\partial c_2^2}\right)_{p,T} / (L/T)$$

$$= -\frac{RT^2 c_2}{S_{cc}^{(0)} L}$$

Hence liquidus curve depends crucially on $\langle(\Delta c)^2\rangle$.

Here L is a generalized concentration dependent latent heat defined by

$$\frac{L}{T} = \frac{L_{10}}{T} + \int_{T_1}^{T} \frac{\Delta c_{p10}}{T}\, dT - \left(\frac{\partial}{\partial T}\left[RT \ln(\gamma_1(1-c_2))\right]\right)$$

eqn

γ_1 being the activity.

If we now

(i) Expand Δc_{p10} about T_1 & neglect higher terms than the first

(ii) Calculate activity γ_1 from conformal soln theory

($RT \ln \gamma_1 \doteq w c^2$)

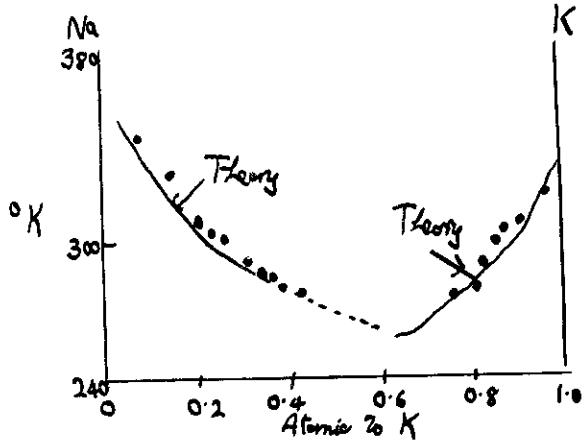
then

$$c(t) - 1 = \left[c_{ideal} - 1\right] \exp\left(-Wc^2/t\right)$$

$$t = T/T_1, \quad W = \frac{w}{RT_1}.$$

Use value from partial structure factor $\frac{w}{RT_1}^{Na} = 1{\cdot}1$.

Hence get theory of liquidus curves of eutectic mixture



Relation of regular solution theory of liquid metal alloys to Miedema's work

We shall see that interchange energy w in conformal soln theory is calculable from properties of reference liquid ($\phi(r)$ and $g(r)$ solely). But how to find ref liquid for a given alloy system remains question?

Therefore, of interest to point out that we can use Miedema's work (@ Miedema, de Chatel & de Boer 1980) to express w in an a–b alloy in terms of:

(i) the boundary electron densities n_a and n_b in pure metals a and b

and

(ii) the electronegativity difference (referred to earlier in Prof. Enderby's lectures)

Since W can be estimated, as we have discussed, from thermodynamic (activity) data and from phase diagrams, link can be forged between SOLUTION theory and electron theory of metals more directly (though less fundamentally) that via alloy pair potentials.

If V_a and V_b are the atomic volumes of pure metals a and b, then from Miedema's calculations of the heat of solution of i in j (say $\Delta H_s(i \text{ in } j)$, we can set

$$W = \frac{1}{2}\left[\Delta H_s(a \text{ in } b) + \Delta H_s(b \text{ in } a)\right]$$

This yields ← Miedema expressions which can't derive here

$$W = \frac{V_a^{2/3} + V_b^{2/3}}{n_a^{-1/3} + n_b^{-1/3}}\left[-P\left(n_a^{\frac{1}{3}} - n_b^{\frac{1}{3}}\right)^2 + Q\left(x_a - x_b\right)^2\right]$$

$n_a^{\frac{1}{3}}$; $(x_a - x_b)$: Electronegativity difference

where P and Q are almost constant, through a wide class of alloys.

Thus, LINK between n_a and n_b (obtainable from electron theory of PURE metals, the electronegativity difference $(x_a - x_b)$ and interchange energy W of SOLUTION theory.

Mixtures of 2 alkalis: numerical consequences

Alloy (ab)	W (units are kJ/g at. solute)	Expt.
NaK	5·5	2·9
Cs K	0·0	0·45
(NaCs)	10·0	5·0
RbCs	0·0	−0·5
K Rb	0·0	0·5
NaRb	7·5	5·4

not confirmed, as we shall see below.

Actually W obtained by this method is ~ factor of 2 too large for NaK: unacceptable in calculating $S_{cc}(0)$. Refinements of Miedema's work needed ∴ but GROSS TRENDS are evident.

Flory's (1942) model for Gibbs free energy of mixing

Gibbs free energy of mixing according to Flory has form

$$\Delta_m G = N k_B T \left[c \ln \phi + (1-c) \ln (1-\phi) \right] + N g(c) w$$

where the last term in energy of mixed, the conc. dep. not being written out explicitly

The modification in entropy term is that ϕ is the concentration by volume of species 1. If v_1 & v_2 are the partial molar volumes, then ϕ is given by

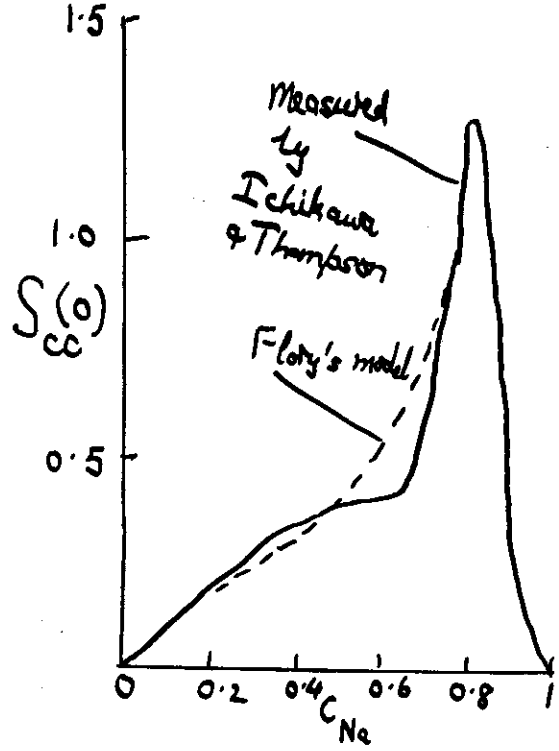
$$\phi = \frac{c v_1}{c v_1 + (1-c) v_2}$$

We use this model in Na–Cs because $v_2/v_1 = 3$. We get

$$S_{cc}(0) = c(1-c) \left[1 + c(1-c)\delta^2 + c(1-c) g''(c) \frac{w}{k_B T} \right]^{-1}$$

[in terms of δ, $\phi = c + c(1-c)\delta$] (size factor.

Liquid Na–Cs alloy (large size difference)



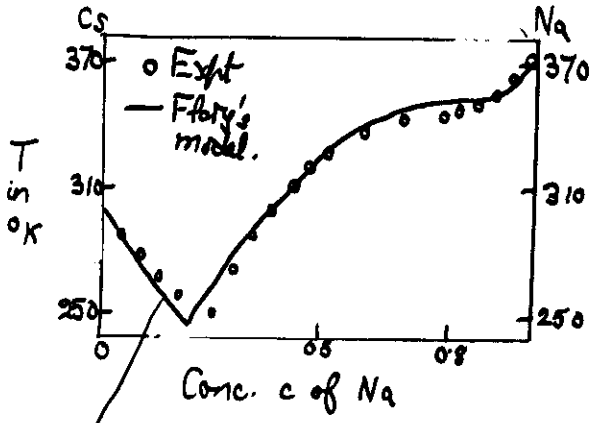
$\frac{w}{RT} = 1.14$ gives good fit.

Flory proposed a modification of regular soln model

$c(1-c) \rightarrow g(c)$ — not symm. around $c = \frac{1}{2}$.

Position of peak depends on balance between size ratio v_2/v_1 and interchange energy w.

Liquidus curves of Na–Cs



From $S_{cc}(0)$ calcd from Flory's model

Since we saw that slope of liquidus curve was

$$\frac{\Delta T}{\Delta c} = -\frac{RT^2 c}{S_{cc}(0) L}$$

we could know from rather flat portion of liquidus curve around $c = 0{\cdot}8$ that there was a huge peak in $S_{cc}(0)$ there.

$\underset{\sim}{k}$-dependent structure factors $S_{NN}(k)$, $S_{cc}(k)$, $S_{Nc}(k)$

Two approaches will be developed:

(i) General, but so far hard to apply

(ii) Conformal solution theory

(One simple result – namely $S_{cc}(k)$, since it depends, as with w, only on $g(r)$ and $\phi(r)$ of reference liquid.)

We shall tackle (i) first, indicating one (first-order) way to use experimental data on $S_{11}(k)$, $S_{12}(k)$ and $S_{22}(k)$ discussed by Prof. Enderby, to get an estimate of pair force curves in a–b mixtures.

As for (ii), there are expressions for $S_{cc}(k)$ – but only valid in limits of validity of CONFORMAL SOLUTION theory.

Consider binary liquid mixture : N atoms of type a at $\underset{\sim}{R}_1 \cdots \underset{\sim}{R}_N$: n atoms b at $\underset{\sim}{r}_1 \cdots \underset{\sim}{r}_n$.

For a configuration in which atom a is at $\underset{\sim}{R}_1$ and atom b is at $\underset{\sim}{r}_1$, write down an eqn for the mean force $-\partial U_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1)/\partial \underset{\sim}{R}_1$ acting on atom a.

We have direct interaction $-\partial \phi_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1)/\partial \underset{\sim}{R}_1$ and secondly a contribution from rest of system.

Calc. of INDIRECT contribution

Consider second atom of type a at $\underset{\sim}{R}_2$ acting with a force $-\partial \phi_{aa}(\underset{\sim}{R}_1 - \underset{\sim}{R}_2)/\partial \underset{\sim}{R}_1$ and a second atom of type b at $\underset{\sim}{r}_2$, with resulting force $-\partial \phi_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_2)/\partial \underset{\sim}{R}_1$. We must then sum these contributions, multiply by the probability of this 4 atom configuration :

$$\rho^{(4)}_{abab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1 \underset{\sim}{R}_2 \underset{\sim}{r}_2)/\rho^{(2)}_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1)$$

and finally integrate over locations of 2nd type of atom. Result is

$$-\frac{\partial U_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1)}{\partial \underset{\sim}{R}_1} = -\frac{\partial \phi_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1)}{\partial \underset{\sim}{R}_1} - \int \frac{\rho^{(4)}_{abab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1 \underset{\sim}{R}_2 \underset{\sim}{r}_2)}{\rho^{(2)}_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1)} \times \left[\frac{\partial \phi_{aa}(\underset{\sim}{R}_1 - \underset{\sim}{R}_2)}{\partial \underset{\sim}{R}_1} + \frac{\partial \phi_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_2)}{\partial \underset{\sim}{R}_1} \right] d\underset{\sim}{R}_2 d\underset{\sim}{r}_2$$

Since three atom correlations $\rho^{(3)}$ are related to $\rho^{(4)}$ by

$$\rho^{(3)}_{aba}(\underset{\sim}{R}_1 \underset{\sim}{r}_1 \underset{\sim}{R}_2) = \int \rho^{(4)}_{abab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1 \underset{\sim}{R}_2 \underset{\sim}{r}_2) d\underset{\sim}{r}_2$$

and

$$\rho^{(3)}_{abb}(\underset{\sim}{R}_1 \underset{\sim}{r}_1 \underset{\sim}{r}_2) = \int \rho^{(4)}_{abab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1 \underset{\sim}{R}_2 \underset{\sim}{r}_2) d\underset{\sim}{R}_2,$$

we find

$$-\frac{\partial U_{ab}}{\partial \underset{\sim}{R}_1}(\underset{\sim}{R}_1 \underset{\sim}{r}_1) = -\frac{\partial \phi_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1)}{\partial \underset{\sim}{R}_1} - \int \frac{\rho^{(3)}_{aab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1 \underset{\sim}{R}_2)}{\rho^{(2)}_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1)} \frac{\partial \phi_{aa}(\underset{\sim}{R}_1 - \underset{\sim}{R}_2)}{\partial \underset{\sim}{R}_1} d\underset{\sim}{R}_2$$

$$- \int \frac{\rho^{(3)}_{abb}(\underset{\sim}{R}_1 \underset{\sim}{r}_1 \underset{\sim}{r}_2)}{\rho^{(2)}_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_1)} \frac{\partial \phi_{ab}(\underset{\sim}{R}_1 \underset{\sim}{r}_2)}{\partial \underset{\sim}{R}_1} d\underset{\sim}{r}_2 .$$

For two atoms of type a, we can write a similar force eqn.

Exact, but can't make progress without use of the Kirkwood-type approximation. Invert problem, and ask how ϕ_{aa} etc might be extracted. If ϕ_{aa} & U_{aa} not very different, replace ϕ_{aa} in 'indirect' term by U_{aa}. Can then get formulae (admittedly limited range of validity

These are :

$$\phi_{aa}(R) = U_{aa}(R) + \frac{k_B T \rho_a}{8\pi^3 \rho^2} \int [S_{aa}(k) - 1]^2 \exp(i \underset{\sim}{k} \cdot \underset{\sim}{R}) d\underset{\sim}{k}$$

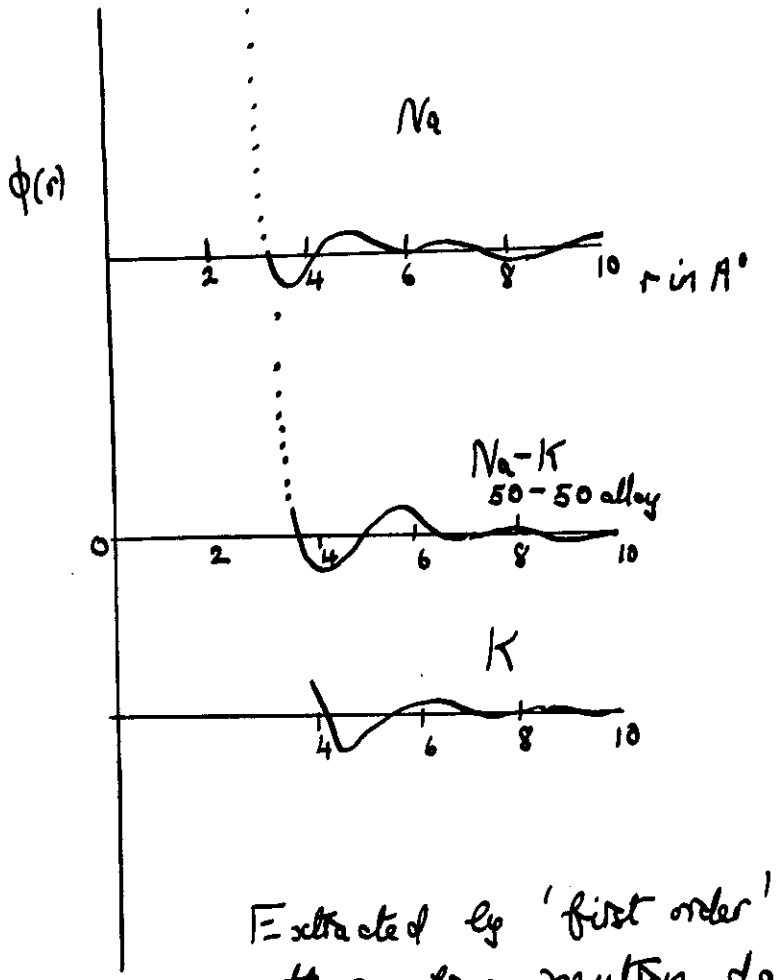
$$+ \frac{k_B T \rho_b}{8\pi^3 \rho^2} \int [S_{ab}(k) - 1]^2 \exp(i \underset{\sim}{k} \cdot \underset{\sim}{R}) d\underset{\sim}{k}$$

and

$$\phi_{ab}(R) = U_{ab}(R) + \frac{k_B T \rho_a}{8\pi^3 \rho^2} \int [S_{aa}(k) - 1] [S_{ab}(k) - 1] \exp(i \underset{\sim}{k} \cdot \underset{\sim}{R}) d\underset{\sim}{k}$$

$$+ \frac{k_B T \rho_b}{8\pi^3 \rho^2} \int [S_{ab}(k) - 1][S_{bb}(k) - 1] \exp(i \underset{\sim}{k} \cdot \underset{\sim}{R}) d\underset{\sim}{k}.$$

Would be of interest, it would seem, to use measured structure data to estimate ϕ_{aa}, ϕ_{ab} and a similar eqn for ϕ_{bb}. But could only be quantitative if $\phi_{aa} \sim U_{aa}$ etc !!.



Extracted by 'first order' theory from neutron data of Page on $S_{NN}(k)$ for 50-50 % alloy, and from Rainfield, Wiser & Wellendorf for pure Na & K.