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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

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STRUCTURE AND FORCES IN LIQUIDS AND LIQUID MIXTURES

Summary of Lecture V

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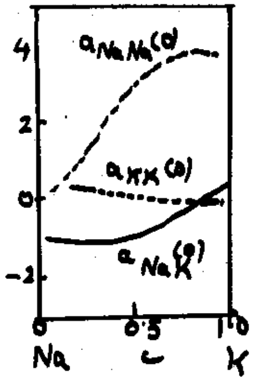
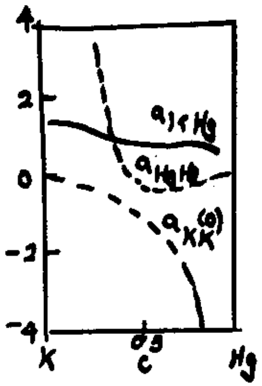
McAlister & Turner
(J Phys F2, L51, 1972)



Na–K
at 100°C



K–Hg
at 320°C

(Evaluated from thermodynamic data on activities)

Relation of fluctuations $\langle(\Delta c)^2\rangle$ etc
to thermodynamic quantities

(Bhatia & Thornton, Phys Rev B2, 3006, 1970)

Let N_1 and N_2 denote mean number of atoms of 2 types in a given macroscopic volume Ω. Let ΔN_1 & ΔN_2 denote the instantaneous deviation from the mean

The probability of these deviations (see, for example, the books by R. C. Tolman or T. L. Hill) is given by ($i,j = 1, 2$)

$$w = w_0 \exp\left(-\sum_{i,j} \frac{F_{ij}\, \Delta N_i \Delta N_j}{2k_B T}\right)$$

where w_0 is the normalization constant and

$$F_{ij} = \left.\frac{\partial^2 F}{\partial N_i \partial N_j}\right|_{\Omega,T} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,\Omega,N}$$

$$= \left(\frac{\partial \mu_j}{\partial N}\right)_{T,\Omega,N} = F_{ji}.$$

$$\mu_i = \left.\frac{\partial F}{\partial N_i}\right|_{T,\Omega,N'} = \left.\frac{\partial G}{\partial N_i}\right|_{T,p,N'}$$

μ_i is chemical potential of species i, and subscript N' indicates that a N_i not being differentiated is held fixed.

From the property of the Gaussian distributions, we have

$$\langle \Delta N_i \Delta N_j \rangle = k_B T (F^{-1})_{ij}$$

where $(F^{-1})_{ij}$ is evidently the ij element of the inverse matrix of F_{ij}.

Now

$$\left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,\Omega,N'} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,p,N'} + \frac{v_i v_j}{\Omega K_T}$$

where $v_i = \left(\frac{\partial \Omega}{\partial N_i}\right)_{T,p,N}$ is the partial molar volume for the species i and

$$\Omega = N_1 v_1 + N_2 v_2 .$$

Hence

$$\sum_{ij} F_{ij} \Delta N_i \Delta N_j = \frac{1}{\Omega K_T}\left(v_1 \Delta N_1 + v_2 \Delta N_2\right)^2 + \sum_{ij} \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,P,N'} \Delta N_i \Delta N_j$$

Now we use the Gibbs–Duhem relns in form for 2 components.

$$\sum_{i=1}^{2} N_i \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,P,N'} = 0 , \; j = 1, 2$$

to simplify sum, and remember that

$$\Delta N = \Delta N_1 + \Delta N_2 \quad \text{and}$$

$$N \Delta c = (1-c)\Delta N_1 - c \Delta N_2$$

one obtains

$$\sum_{ij} F_{ij} \Delta N_i \Delta N_j = \left(\frac{\Omega}{K_T N^2}\right)\left[\Delta N + N \Delta c \, \delta\right]^2 + B(\Delta c)^2$$

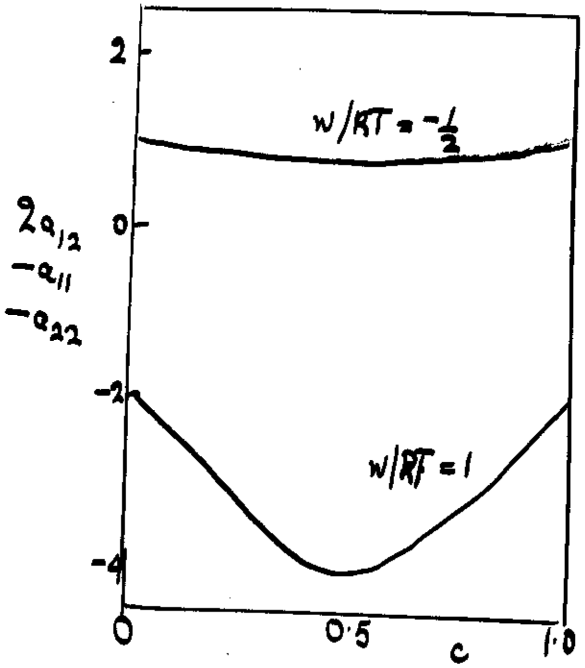
where δ is given by

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

and

$$B = \left(\frac{N^4}{N_2^2}\right)\left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,p,N'} = \left(\partial^2 G / \partial c^2\right)_{T,p,N} .$$

Thus, the fluctuations we want $\langle (\Delta c^2) \rangle$ $\langle (\Delta N)^2 \rangle$ and $\langle \Delta N \Delta c \rangle$ can be written in terms of δ (size factor), K_T and $(\partial^2 G/\partial c^2)$.



Exptl data of McAlister and Turner (1972) for liquid Na-K (100°C).

At $c = 0.5$

$$a_{11} = a_{NaNa} = 2.9, \quad a_{22} = a_{KK} = 0.05,$$
$$a_{12} = a_{NaK} = -0.95$$

yielding

$$2a_{12} - a_{11} - a_{22} = -4.85.$$

We set the empirical value of w as

$$\frac{w}{RT} = 1.10$$

(this agrees with exptl data on heats of mixing : Hultgren et al, 1963)

We can get δ from the theory using the fact that

$$\text{Volume} \equiv \left(\frac{\partial G}{\partial p}\right)_T = (1-c)v_1^\circ + c\,v_2^\circ + c(1-c)w'$$

$$w' = \left(\frac{\partial w}{\partial p}\right)_T$$

Molar volumes of pure species.

Compress. also. (involves w''). Vary w' & w'' to see effect.

Partial structure factors in long wavelength limit as fns of conc. of K in liquid Na-K alloys at 100°C.