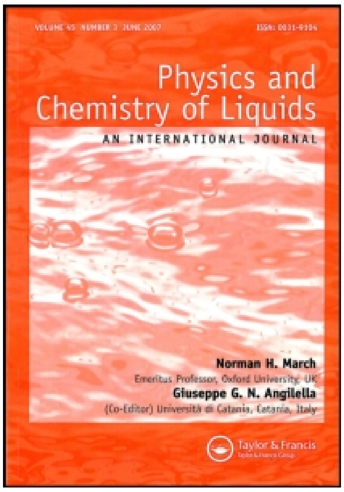

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Osmotic Pressure Related to Concentration Fluctuations, With Application to Liquid Metal Alloys

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Osmotic Pressure Related to Concentration Fluctuations, With Application to Liquid Metal Alloys

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An integral equation is first set up which allows the osmotic pressure to be calculated from knowledge of (a) the concentration fluctuations and (b) the equations of state of the two pure liquids 1 and 2 which are constituents of the binary 1–2 mixture. The method is illustrated by approximate numerical calculations on a variety of liquid binary mixtures, including Na–Ga and Na–Cd under pressure.

1 INTRODUCTION

Although first principles calculations of force laws in solid and liquid metal alloys are by now possible from electron theory, simpler descriptions remain of interest for many practical purposes. In particular, chemical solution theories continue to merit further study. It was shown, for example, by Bhatia *et al.*,[1] that regular solution theory provided a valuable framework for interpreting the concentration fluctuations, as well as the liquidus curves,[2] of liquid Na–K alloys.

Later work by Bhatia and March[3] focussed on the use of Flory's model[4] for treating liquid Na–Cs alloys, in which the ratio of the atomic volumes is near to a factor of 3. It has been known for a long time that, while regular solution theory can, roughly, accommodate volume ratios of about 2, that for Na–K, it rapidly breaks down when larger size differences are involved.

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This work on Na–Cs has been taken further, for example in the study of Neale and Cusack[5] and very recently by Singh and Bhatia.[6]

The present paper is primarily concerned with the osmotic pressure as a useful tool linking the thermodynamic properties of binary liquid mixtures with the thermodynamics of the pure components. While this can be said, in essence, to be the aim of all solution theories, it is presently the case, almost always, that the existing relations are more restrictive; they use only information about the pure liquids 1 and 2 in a liquid binary 1–2 mixture at the same thermodynamic state, p, T say, as that of the mixture.

It was recently pointed out by one of us,[7] in placing an earlier suggestion of Hammel[8] on a rigorous thermodynamic footing, that a more powerful approach to solution theories might be to exploit the knowledge of the thermodynamic properties of the pure liquids 1 and 2 as a function of pressure, at the temperature T say of the alloy experiments. The tool that then proves convenient, as Hammel[8] originally suggested, is the osmotic pressure.

The outline of the present paper is as follows. In Section 2 below, we outline the theory relating osmotic pressure to concentration fluctuations in the solution, and to the equations of state of the pure liquids 1 and 2. In Section 3, this approach is then applied directly to liquid Na–Ga and Na–Cd alloys, for which there are observations on the pressure dependence of the concentration fluctuations, via activity coefficient measurements.

To compare osmotic pressures derived from this approach with model predictions, Section 4 is briefly concerned with the "conformal" solutions Na–K, Ar–Kr and Kr–Xe. Then in Section 5, Flory's model, appropriate for the case when the size difference between the components is large, is considered in relation to data on liquid Na–Cs. Section 6 constitutes a summary, together with a brief discussion of the likely role of osmotic pressure in solution theories.

2 RELATION BETWEEN OSMOTIC PRESSURE AND CONCENTRATION FLUCTUATIONS

Paralleling the argument presented in Ref. 7, we express the Gibbs free energy G of the mixture at concentration x as

$$G = (1 - x)\mu_1 + x\mu_2. \tag{2.1}$$

The condition for osmotic equilibrium between pure component 1, with chemical potential μ_1^0, and the solution, is

$$\mu_1(p, T, x) = \mu_1^0(p - \Pi_1, T) \tag{2.2}$$

where Π_1 is the appropriate osmotic pressure. Similarly, for osmotic equilibrium between pure component 2 and the solution we can write the corresponding result

$$\mu_2(p, T, x) = \mu_2^0(p - \Pi_2, T). \tag{2.3}$$

At this stage we note that the Gibbs–Duhem relation permits one to write[9]

$$\mu_1 = G - x\frac{\partial G}{\partial x} \tag{2.4}$$

and

$$\mu_2 = G + (1 - x)\frac{\partial G}{\partial x}. \tag{2.5}$$

The concentration fluctuations $(\Delta x)^2 \equiv S_{xx}$ say, are related to the Gibbs free energy by[1–3]

$$S_{xx} = \frac{Nk_B T}{(\partial^2 G/\partial x^2)_{p,T}} \tag{2.6}$$

and hence one can write from Eqs (2.4) and (2.6):

$$\frac{\partial \mu_1}{\partial x} = -x\frac{\partial^2 G}{\partial x^2} = -x\frac{Nk_B T}{S_{xx}}. \tag{2.7}$$

Similarly, from Eqs (2.5) and (2.6) one finds

$$\frac{\partial \mu_2}{\partial x} = (1 - x)\frac{\partial^2 G}{\partial x^2} = \frac{(1 - x)Nk_B T}{S_{xx}}, \tag{2.8}$$

equations (2.7) and (2.8) being an alternative way of ensuring the Gibbs–Duhem relation.

At this stage, we return to the condition of osmotic equilibrium (2.2), and introducing this into Eq. (2.7) leads to

$$\frac{\partial \Pi_1}{\partial x}\mu_1^{0\prime}(p - \Pi_1, T) = \frac{xNk_B T}{S_{xx}} \tag{2.9}$$

the prime denoting differentiation with respect to the total argument $p - \Pi_1$. But this derivative $\mu_1^{0\prime}$ is simply the volume $V_1^0(p - \Pi_1, T)$ of pure liquid 1, no longer though at the thermodynamic state p, T of the mixture measurements, but at the different thermodynamic state $p - \Pi_1$, T. Hence one can write

$$\frac{\partial \Pi_1}{\partial x} = \frac{xNk_B T}{S_{xx}V_1^0(p - \Pi_1, T)} \tag{2.10}$$

This first-order differential equation is readily integrated to yield

$$\Pi_1(x) = \int_0^x \frac{xNk_BT\,\mathrm{d}x}{S_{xx}V_1^0(p - \Pi_1, T)} \tag{2.11}$$

This Eq. (2.11) is plainly an implicit equation from which the osmotic pressure Π_1 can be determined if one is given the concentration fluctuations S_{xx} and the equation of state of pure liquid 1. Equation (2.11) plus a corresponding equation determining the osmotic pressure Π_2 in Eq. (2.3) constitute the basis for the calculations presented in Sections 3–5 below.

In order to make the application of Eq. (2.11) a little more transparent, before the detailed use in Sections 3–5 below, let us make the approximations in the right-hand side of Eq. (2.11) that (i) $S_{xx} = x(1 - x)$, its value in an ideal solution, and (ii) Π_1 can be neglected compared with p. Then one can integrate to find

$$V_1^0\Pi_1 = -Nk_BT\ln(1 - x), \tag{2.12}$$

which is an often quoted result[9] for the osmotic pressure of an ideal solution.

To complete this discussion, we merely note that the corresponding result for Π_2 may be expressed in the form

$$\Pi_2(x) = \int_x^1 \frac{(1 - x)Nk_BT}{S_{xx}V_2^0(p - \Pi_2, T)}. \tag{2.13}$$

The remainder of the paper is concerned with some numerical consequences of these results (2.11) and (2.13) for liquid alkali metal alloys. We stress, though, that these equations are exact consequences of thermodynamics for all binary mixtures.

3 OSMOTIC PRESSURE OF LIQUID Na–Ga AND Na–Cd UNDER EXTERNAL PRESSURE

We stress immediately that Eq. (2.11) will come into its own for liquid mixtures at high external pressure p, over a range of concentration x for which $p - \Pi_1(x) > 0$. Plainly, if S_{xx} is known from experiment, then Eq. (2.11) can be solved iteratively to determine $\Pi_1(x)$, given also the equation of state of the pure substance 1.

To illustrate the nature of the results thereby obtained, Figure 3.1 shows the osmotic pressure of liquid Na–Ga alloys as a function of concentration. Though we have, in fact, plotted curves for both $p = 1$ bar and $p = 500$ bar over the entire range of concentration, using the concentration fluctuation data given in Ref. 10, we have assumed the dependence on x of V_1^0 to be weak compared with the dependence of S_{xx}. In practice, the physical range

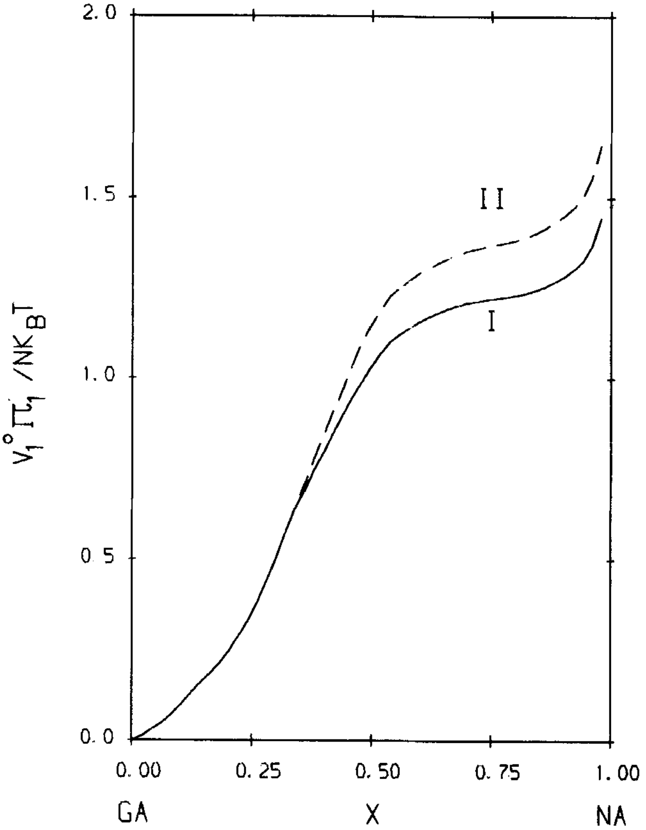

FIGURE 3.1 Osmotic pressure Π_1 for liquid Na–Ga alloys. Curve I is calculated for external pressure equal to 1 atmosphere. Curve II is for $p = 500$ bar. The physically significance range, however, of curve I is near $x = 0$, while that for $p = 500$ bar is for $x < 0.3$. However, the main point made by the curves is that, at external pressures of a few kilobar, the external pressure dependence of the osmotic pressure for concentrations around $x \sim 0.7$ should be considerable. Temperature is 843 K.

of the curves in Figure 3.1 is quite limited; for 500 bar external pressure the range of physical interest is $0 < x \lesssim 0.3$ while for $p = 1$ bar the range is a tiny region only near $x = 0$. It is clear from Figure 3.1 that, to enter the regime where external pressure effects change the osmotic pressure importantly one will have to apply pressures eventually of the order of 1500 to a few thousand bar. However, in this pressure range, our calculations reveal that osmotic pressure will become sensitive to p for $x \sim 0.5$. Clearly, should it eventually prove of interest, plots of $\Pi_2(x)$ can be readily added to Figure 3.1.

Figure 3.2 shows that the situation is rather different for liquid Na–Cd, where we have used the concentration fluctuation data of Ref. 10 again under

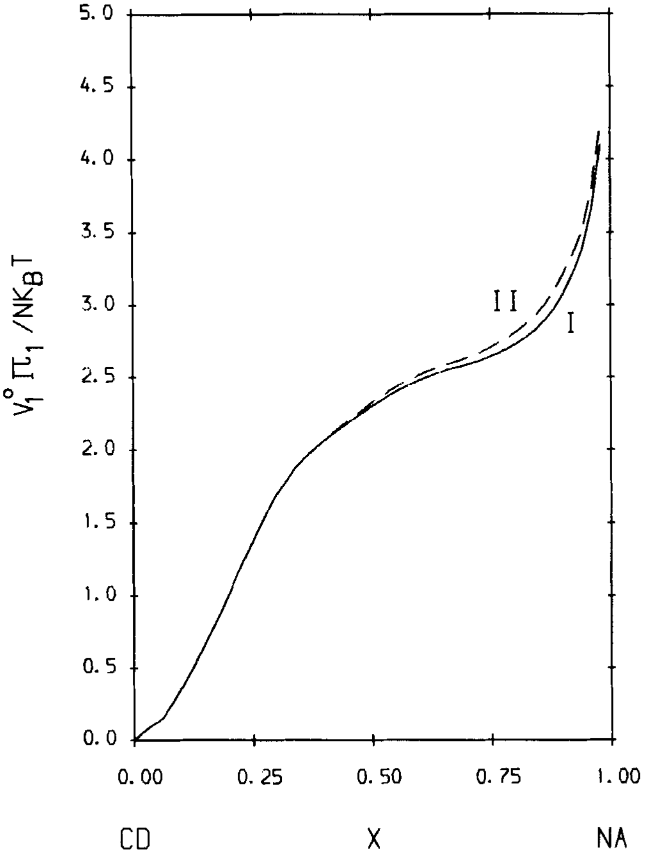

FIGURE 3.2 Same as Figure 3.1 but for liquid Na–Cd alloys at 673 K.

external pressure. Here pressure effects are much smaller and we need not go into further detail in this example.

4 CONFORMAL SOLUTION MODEL COMPARED WITH EXPERIMENT FOR Na–K, Ar–Kr AND Kr–Xe

Briefly, we note that in liquid Na–K alloys, it was shown by Bhatia *et al.*[1] that the observed concentration fluctuations are well represented by

$$S_{xx} = \frac{x(1-x)}{1 - \dfrac{2w}{Nk_BT}x(1-x)}. \tag{4.1}$$

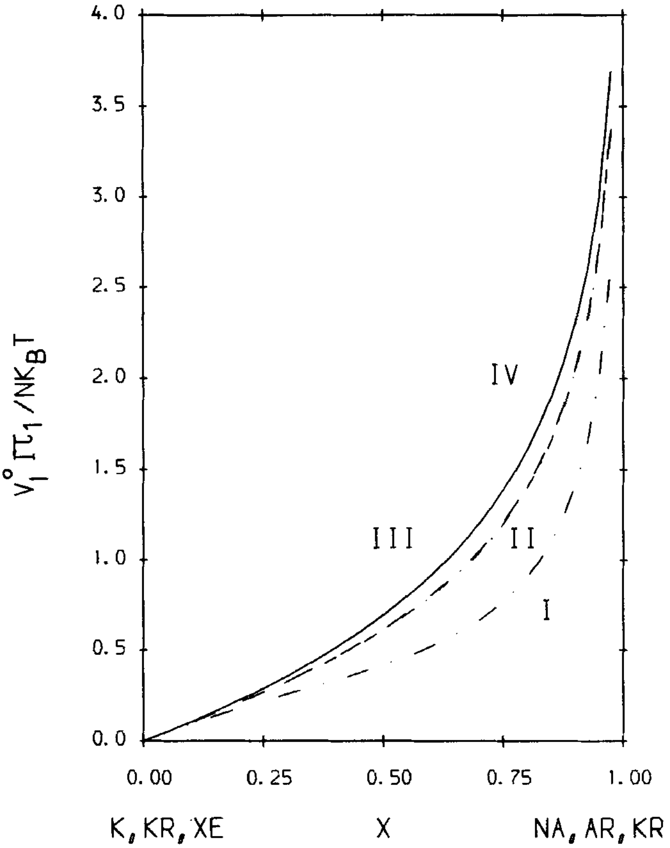

FIGURE 4.1 Curve I Liquid Na–K at 373 K; Curve II Liquid Ar–Kr at 116 K; Curve III Liquid Kr–Xe at 161 K; Curve IV Ideal solution.

The "experimental" results for $\Pi_1(x)$ derived from Eq. (2.11) with measured concentration fluctuations S_{xx} are largely indistinguishable graphically from the results of the conformal solution model. In particular curves II and III cannot be separated graphically.

Curve I of Figure 4.1 shows a plot of $\Pi_1(x)$ for Na–K; the conformal solution results, assuming V_1^0 is independent of x, compared with the relatively strong dependence of S_{xx}, are indistinguishable from experiment.[11] However, the same reservations are applicable to this figure as apply to Figure 3.1; i.e. the physical range of x is very small at atmospheric pressure. We presently know of no measurements of S_{xx} at other pressures for liquid Na–K; however Bhatia *et al.*[12] have given estimates of the way the interchange w in Eq. (4.1) will vary with external pressure. Should experimental data under pressure become available on this system, it will be of interest to use this predicted interchange energy within the conformal solution model.[13]

Also added to Figure 4.1 are results for liquid Ar–Kr and Kr–Xe; similar conclusions obtain. The conformal solution model seems truly excellent for these three mixtures.

5 OSMOTIC PRESSURE IN FLORY'S MODEL

Bhatia and March[3] have given the concentration fluctuations S_{xx} derived from the model originally proposed by Flory,[4] in terms of two parameters, the interchange energy, conveniently written scaled with Nk_BT, namely

$$W = w/Nk_BT \tag{5.1}$$

and the ratio of atomic volumes $r_B/r_A = r$, embodied in the parameter β defined by

$$\beta = (r - 1)/r \tag{5.2}$$

The result given by Bhatia and March for S_{xx}, the concentration fluctuations, is then

$$S_{xx} = \frac{x(1 - x)}{1 - x(1 - x)F(x)} \tag{5.3}$$

where $F(x)$ is given by

$$F(x) = \frac{x + [(2/\beta^3)(1 - \beta)W - (1/\beta)]}{[(1/\beta) - x]^3}. \tag{5.4}$$

We note at this point that, if we take the limit $\beta \to 0$ in Eq. (5.4), then both numerator and denominator have leading terms of order β^{-3} and $F(x) \to 2W$ as $\beta \to 0$, leading back to regular solution theory in the form of Eq. (4.1). The important feature to emphasize at this point is that, while regular solution theory is dependent only on the concentration x through the combination $x(1 - x)$, and therefore the concentration fluctuations are symmetrical about $x = \frac{1}{2}$ (see Section 4 above for Na–K), for the Flory model this is no longer true, a situation which is essential to describe experiments on Na–Cs.[5] Following the same procedure as above, we insert the approximation for S_{xx} defined by Eqs. (5.3) and (5.4) into Eq. (2.11) and again assume in the right-hand side that Π_1 can be neglected compared with p. Then we find the result

$$\frac{V_1^0\Pi_1(x)}{Nk_BT} = -\ln(1-x) - \int_0^x \frac{x^2}{[\beta^{-1}-x]^3}\,\mathrm{d}x - \int_0^x \frac{x\Gamma}{[\beta^{-1}-x]^3}\,\mathrm{d}x;\ \Gamma = \left[\left(\frac{2}{\beta^3}\right)(1-\beta)W - \beta^{-1}\right]. \quad (5.5)$$

This has been evaluated using the values of the parameter $W = 1.14$ at 383 K given by Bhatia and March; the result for $V_1^0\Pi_1/Nk_BT$ being plotted against x in Figure 5.1.

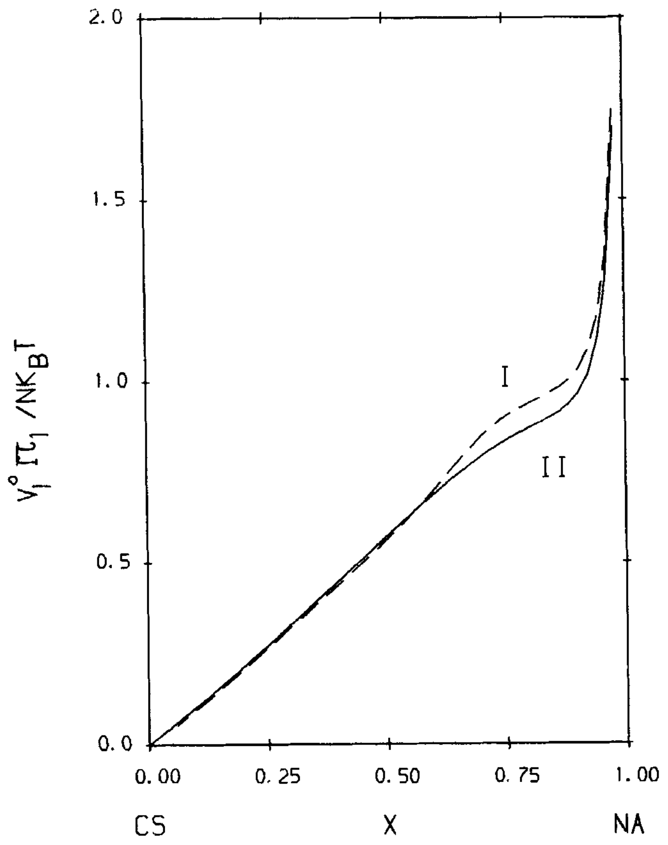

FIGURE 5.1 Osmotic pressure for liquid Na–Cs. Experimental concentration fluctuation data[14] are used to obtain curve I. Flory's model is plotted in curve II. Note that this curve for other than very low concentrations will only be physically realizable at high external pressures; expected to lie in the range of a few kilobar. Temperature is 383 K.

This has then been put back into the right-hand side of Eq. (2.11), the equation of state of pure liquid Na again being employed. The next approximation is thus obtained (see also Appendix 2 for analytical work on the inclusion of Π_1 in the right-hand-side of Eq. (2.11).

6 SUMMARY AND DIRECTIONS FOR FUTURE WORK

We have explored in this paper the nature of the osmotic pressure in a variety of solutions. We have to say that, at the present time, it is not clear to us whether it will technically be feasible to measure the osmotic pressure of liquid metal mixtures, either at atmospheric pressure, or preferably at external pressures of some kbar. If this does become a practical possibility later, then our work indicates that one favourable case to explore would be liquid Na–Ga. Here we expect that, once the range of a few kbar external pressure is reached, there will be appreciable dependence of the osmotic pressure as a function of concentration with external pressure p.

Though less interesting in the present context, we have also briefly considered liquid Na–K, Ar–Kr and Kr–Xe mixtures; here all evidence points to the fact that, for thermodynamic purposes, the conformal solution model is an excellent one. However, we have pointed out that the work of Bhatia *et al.* indicates rather clearly that the interchange energy in the conformal solution Na–K must vary significantly with external pressure, and this point will be well worth testing experimentally in the future.

The Flory model is briefly considered in the present context in relation to liquid Na–Cs alloys where size differences are too large for conformal solution theory to apply.

Finally, the results of this paper show that the use of osmotic pressure as a tool in solution theories is most likely to come into its own at pressures which, at least for liquid Na–Ga, will be in the range of several kbar.

Acknowledgement

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Appendix 1 Osmotic pressure and compressibility of liquid mixture

For use in the calculations in Section 3, we summarize here the exact thermodynamics of the quantity VK_T for the liquid mixture, V being the mixture volume and K_T its isothermal compressibility.[7]

From Eqs (2.1)–(2.3), one can evaluate $V = (\partial G/\partial p)_{T,x}$ and the isothermal compressibility from

$$K_T = -V^{-1}(\partial V/\partial p)_{T,x}. \tag{A1.1}$$

The result for the desired product VK_T can be written:

$$\begin{aligned} -VK_T &= (\partial V/\partial p)_{T,x} \\ &= (1-x)\left(-\frac{\partial^2\Pi_1}{\partial p^2}\right)\mu_1^{0\prime}(p-\Pi_1, T) \\ &\quad + (1-x)\left(1-\frac{\partial\Pi_1}{\partial p}\right)^2(-)(VK_T)_{1,p-\Pi_1} \\ &\quad + x\left(-\frac{\partial^2\Pi_2}{\partial p^2}\right)\mu_2^{0\prime}(p-\Pi_2, T) \\ &\quad + x\left(1-\frac{\partial\Pi_2}{\partial p}\right)^2(-)(VK_T)_{2,p-\Pi_2}. \end{aligned} \tag{A1.2}$$

This result is the exact version of the Hammel proposal summarized in

Eq. (1) of Ref. 7. This proposal is evidently correct when the pressure derivatives of the osmotic pressure are negligible.

Appendix 2 Approximate solution of integral Eq. (2.11) for osmotic pressure by low order Taylor expansion

As discussed especially in Section 3, the integral Eq. (2.11) for the osmotic pressure Π_1 can be solved by iteration, given the concentration fluctuations S_{xx} as a function of concentration x and the equation of state of pure liquid 1.

We have discussed examples in which Π_1 is neglected relative to p in the integral term in Eq. (2.11); this evidently reduces the integral equation for Π_1 to a formula for the osmotic pressure involving straightforward quadrature.

In this same spirit, it is of interest to consider including the next term in the Taylor expansion in Π_1 of the quantity $V_1^0(p - \Pi_1, T)$ in Eq. (2.11); this is the purpose of the present Appendix.

Assuming the "correction" term in

$$V_1^0(p - \Pi_1, T) = V_1^0(p, T) - \Pi_1 \frac{\partial V_1^0}{\partial p}(p, T) + \cdots \qquad \text{(A2.1)}$$

is small compared with V_1^0, we can rewrite Eq. (2.10) in the form

$$\frac{\partial \Pi_1(x)}{\partial x} \div \frac{xNk_BT}{S_{xx}V_1^0}[1 - \Pi_1 K_T^{(1)}] \qquad \text{(A2.2)}$$

where $K_T^{(1)}$, the isothermal compressibility in pure liquid 1, has been introduced through Eqs (2.10). Evidently, given explicitly the concentration fluctuations S_{xx} as a function of x, Eq. (A2.2) is a quite explicit first-order linear differential equation to solve for the osmotic pressure Π_1.

Introducing the dimensionless variable y defined by

$$y = \frac{V_1^0 \Pi_1}{Nk_BT} \qquad \text{(A2.3)}$$

and the parameter γ given by

$$\gamma = \frac{Nk_B T K_T^{(1)}}{V_1^0} \tag{A2.4}$$

we find the reduced form of Eq. (A2.2) to be

$$\frac{\partial y}{\partial x} + \frac{\gamma x}{S_{xx}} y = \frac{x}{S_{xx}}. \tag{A2.5}$$

This equation is readily solved by means of the integrating factor $\exp(\gamma \int x/S_{xx}\, \mathrm{d}x)$, to yield

$$y = +\gamma^{-1} + K \exp\left(-\gamma \int_0^x \frac{x}{S_{xx}} \mathrm{d}x\right) \tag{A2.6}$$

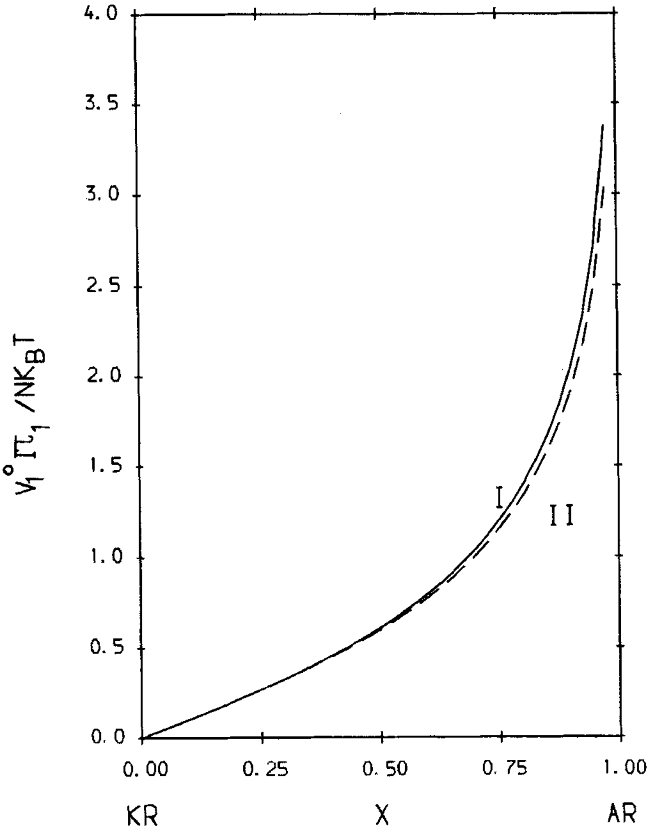

FIGURE A2.1 Osmotic pressure for conformal solution Ar–Kr. Curve I is as in curve II of Figure 4.1. Curve II shows effect of non-zero γ in Eqs (A2.5) and (A2.7). γ is 0.064.

with K the arbitrary constant of integration. As $x \to 0$, $\Pi_1 \to 0$ and hence from the definition (A2.3), y tends to zero. Thus $K = -\gamma^{-1}$, which leads to

$$\gamma y = +1 - \exp\left(-\gamma \int_0^x \frac{x}{S_{xx}} \, \mathrm{d}x\right). \tag{A2.7}$$

As $\gamma \to 0$, this yields

$$y = \int_0^x \frac{x}{S_{xx}} \, \mathrm{d}x \tag{A2.8}$$

which is the limit employed in the analytical examples in the main text.

Equation (A2.7) has also been evaluated numerically for liquid Ar–Kr and is shown in curve II of Figure A2.1, S_{xx} being again taken from conformal solution theory. It should be noted that, in liquid metals just above the melting temperature T_m, the quantity γ is simply the long-wavelength limit of the liquid structure factor $S(k)$; $S(0)|_{T_m}$ being about 0.01–0.03 typically.