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# Partial Coordination Numbers and Flory-Huggins Equation of Binary Hard Sphere Systems with Unequal Hard Sphere Diameters

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Partial radial distribution functions of binary hard sphere systems with strong size difference between the constituting atoms are calculated starting from the Percus-Yevick equation. Partial coordination numbers of nearest neighbours are defined. Empirical relations are found which give partial coordination numbers of an accuracy better than 1% as a function of packing fraction ( $0.2 \leq \eta \leq 0.5$ ), size difference ( $\sigma_2/\sigma_1 \leq 1.44$ ) and composition. Introduction of pairwise interactions between nearest neighbours yields for the enthalpy of mixing approximately the same composition dependence as given by the Flory-Huggins equation, and explains why the numerical value of the "interchange energy" depends on the choice of indexing the constituents.

**KEY WORDS:** Partial coordination numbers. Flory-Huggins equation, interchange energy.

## 1 INTRODUCTION

In many liquid metals and alloys there is no directional covalent bonding between the atoms, and the structure is compact and relatively simple. A good starting point for its description is the structure of a random dense packing of hard spheres. The radial distribution functions describing this structure may be calculated from appropriate equations, and relations exist for a more or less precise determination of thermodynamic properties.<sup>1</sup>

We call  $N = N_1 + N_2$  the total number of particles in a binary alloy. The number of  $i$ - $j$  pairs ( $i, j = 1, 2$ ) is given by  $x_i N \cdot Z_{ij}$  with  $x_i = N_i/N$ . The partial coordination numbers  $Z_{ij}$  corresponds to the number of  $j$  particles surrounding an  $i$  atom. There are  $\frac{1}{2}x_i N Z_{ii}$   $i$ - $i$  pairs. The concept of coordination numbers was adopted from the crystalline state

by many authors though its signification is somewhat problematical for liquids. This concept allows one to formulate the following expression for  $\Delta H$ , if composition independent pairwise interactions  $w_{ij}$  between the particles are postulated:

$$\Delta H = -\left\{\frac{1}{2}x_1Z_{11}w_{11} + x_1Z_{12}w_{12} + \frac{1}{2}x_2Z_{22}w_{22}\right\} + \left\{\frac{1}{2}x_1Z_1^0w_{11} + \frac{1}{2}x_2Z_2^0w_{22}\right\} \quad (1)$$

$\Delta H$  corresponds to the difference between the enthalpy of the solution and the enthalpy of the pure components.  $Z_i^0$  is the total coordination number in pure  $i$ . Total coordination numbers of the alloy are given by  $Z_i = Z_{ii} + Z_{ij}$  and we call  $Z = x_1Z_1 + x_2Z_2$  the mean coordination number.

In the case of substitutional alloys of equally large atoms we have  $Z_1 = Z_2 = Z_i^0 = Z$ . For disordered substitutional solutions  $Z_{ij} = x_j \cdot Z$  and Eq. (1) becomes:

$$\Delta H = -x_1x_2Z(w_{12} - \frac{1}{2}w_{11} - \frac{1}{2}w_{22}) = -x_1x_2Zw \quad (2)$$

$w$  (or  $Zw$ ) is called interchange energy. Equation (2) is based on the assumption that the substitutional solution remains disordered though the interaction between unlike neighbours is different from the mean interaction between like pairs. In reality finite interchange energy will create chemical ordering and the actual partial coordination numbers  $Z_{ij}$  will be larger or smaller than  $Z'_{ij} = x_jZ$ , the partial coordination number of the disordered sample. Hafner, Pasturel and Hicter<sup>2</sup> called "ordering enthalpy,"  $\Delta H_{\text{ord}}$ , the difference between the enthalpy of the ordered and the disordered state at a given composition. In the present, simplified case  $\Delta H_{\text{ord}}$  is given by:

$$\begin{aligned} \Delta H_{\text{ord}} &= -x_1(Z_{12} - x_2Z)w_{12} - \frac{1}{2}x_1(Z_{11} - x_1Z)w_{11} \\ &\quad - \frac{1}{2}x_2(Z_{22} - x_2Z)w_{22} \\ &= x_1x_2Z(w_{12} - \frac{1}{2}w_{11} - \frac{1}{2}w_{22})(1 - Z_{12}/x_2Z) = x_1x_2Zw \cdot \alpha \quad (3) \end{aligned}$$

where  $\alpha = 1 - Z_{12}/(x_2Z)$  is the Warren-Cowley short range order parameter,  $w_{ij}$  and  $w$  are free to change with composition. The authors obtained the total  $\Delta H$  by adding an electronic gas contribution to  $\Delta H_{\text{ord}}$ . It seems interesting to note that  $\Delta H_{\text{ord}}$  given in Eq. (3) will always be negative, irrespective of whether the system is of the segregating ( $\alpha > 0$ ,  $w < 0$ ) or of the compound forming type ( $\alpha < 0$ ,  $w > 0$ ).

The situation becomes much more complicated if the hard spheres differ in size. The total coordination numbers  $Z_1$  and  $Z_2$  will be different and composition dependent. The  $Z_{ij}$  of a disordered solution are no longer given by  $x_jZ_i$ . This is why neither the Warren-Cowley

short-range parameter  $\alpha$  nor the corresponding parameter for non-substitutional alloys of equal size atoms which were introduced by Cargill and Spaepen<sup>3</sup> are helpful for describing such systems. A relation frequently used for calculating  $\Delta F$ , the free energy of mixing, is the Flory-Huggins (FH) equation. Examples for its application were recently given by Ruppertsberg<sup>4</sup>:

$$\Delta F_{\text{FH}} = RT(x_1 \ln \Phi_1 + x_2 \ln \Phi_2) - x_1 \Phi_2 w_{\text{FH}} \quad (4)$$

$\Phi_i$  is the idealized volume fraction:  $\Phi_i = x_i V_i^0 / (x_1 V_1^0 + x_2 V_2^0)$ ,  $V_i^0$  being the molar volume of the pure component  $i$ . The larger atoms are labelled "2."  $\Delta F$  of noninteracting hard-sphere systems is given by the Mansoori<sup>5</sup> equation:

$$\Delta F_{\text{HS}} = -T(\Delta S_{\text{gas}} + S_C + \Delta S_\eta + S_\sigma) \quad (5)$$

$\Delta S_{\text{gas}}$  represents the ideal gas entropy,  $S_C$  is the ideal entropy of mixing. The terms  $\Delta S_\eta$  and  $S_\sigma$  are the packing and misfit contributions, respectively. It has been observed by Visser *et al.*<sup>6</sup> and by Neale and Cusack<sup>7</sup> that the first term on the right side of Eq. (4) corresponds to  $\Delta S_{\text{gas}} + S_C$  of Eq. (5) if  $\Phi_i$  is calculated with the real molar volume instead of  $x_1 V_1^0 + x_2 V_2^0$ . Recently<sup>4</sup> the enthalpy term  $-x_1 \Phi_2 w_{\text{FH}}$  of Eq. (4) is added to Eq. (5) for describing systems of interacting hard spheres. In this paper simple relations for  $Z$  and  $Z_{ij}$  will be deduced, starting from the empirical observation<sup>4</sup> that  $Z_{ii}/\Phi_i$  varies almost linearly with  $\Phi_j$ , and the signification of the FH enthalpy term will be explained. A subsequent paper will deal with chemical order.

## 2 HARD SPHERE FORMALISM AND COORDINATION NUMBERS

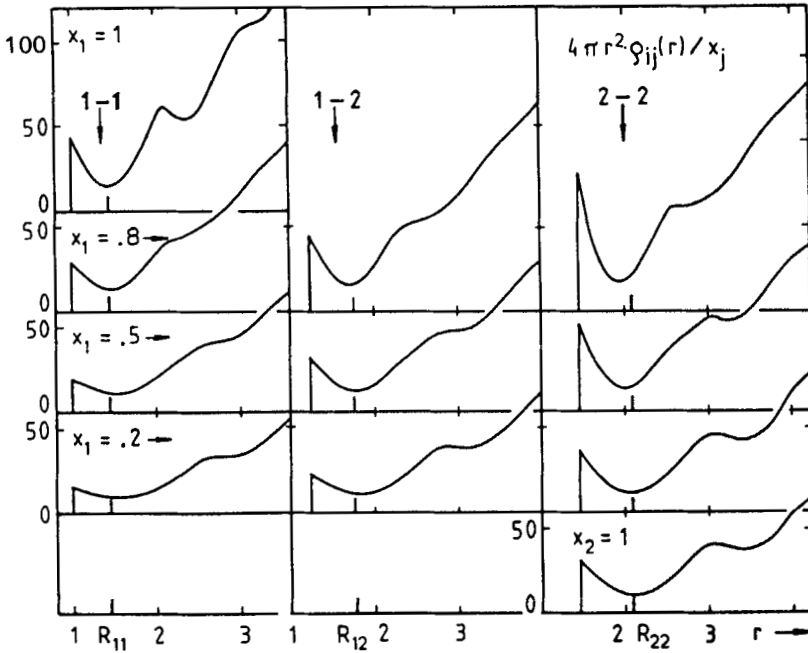
The variables chosen for calculating the structure data are the packing fraction  $\eta$  ( $0.2 \leq \eta \leq 0.5$ ), the hard sphere diameter  $\sigma_i$  ( $\sigma_2/\sigma_1 \leq 1.442$ ) and  $\Phi$ . We discuss first the results obtained for  $\eta = 0.45$ . This packing fraction and  $\sigma_2/\sigma_1 = 1.442$  are close to the values inserted by Ruppertsberg<sup>4</sup> for calculating HS-structure data for comparison with neutron diffraction data of liquid Li/Ba alloys.

The partial structure factors were calculated using the Percus-Yevick approximation. A corresponding computer program is given in Waseda's book.<sup>8</sup> Fourier transformation<sup>4</sup> yields the partial radial distribution functions  $4\pi r^2 \rho_{ij}(r)$  which give the probability per unit volume of finding the centre of a  $j$  particle at distance  $r$  from the centre of an  $i$  sphere. The curves obtained in this way agree almost perfectly with

Monte Carlo results.<sup>4</sup>  $4\pi r^2 \rho_{ij}(r)/x_j$  curves for  $x_1 = 0.2, 0.5, 0.8$  and for the pure components are given in Figure 1. For substitutional alloys these curves would all be identical. In the present case they are indistinguishable only for a given composition at large  $r$ , and very different for small distances. The atomic density is much smaller in the vicinity of the smaller particles. Because nearest neighbours are not separated from the rest of the curves in Figure 1, there is no unique definition for the coordination numbers. We will use the following relation:

$$Z_{ij} = 4\pi \int_{\sigma}^{R_{ij}} r^2 \rho_{ij}(r) dr \quad (6)$$

with  $R_{ij} = 0.72(\sigma_i + \sigma_j)$ . These distances which are indicated by vertical bars in Figure 1 correspond to the position of the minimum following the first peak in the curves of the pure components given in Figure 1 and they are close to the position of the minimum for the corresponding



**Figure 1** Radial distribution functions of the pure components ( $x_1 = 1, x_2 = 1$ ) and relative partial radial distribution functions for  $x_1 = 0.8, 0.5$  and  $0.2$ . The vertical bars indicate the values of  $R_{ij}$ , limiting the first coordination shells.

partial curves of the alloys. The coordination numbers may directly be obtained from the Faber Ziman partial structure factors  $a_{ij}(q)$ . Using  $S_{ii}(q) = x_i a_{ii}(q) + x_j$  and  $S_{ij}(q) = x_j a_{ij}(q) + x_i$  one obtains:

$$Z_{ij} = 4\pi x_j \rho_0 \cdot R_{ij}^3 + (2/\pi) \int ((S_{ij} - 1)/q) \sin(q \cdot R_{ij}) dq \tag{7}$$

$$- 2R_{ij}/\pi \int (S_{ij} - 1) \cos(q \cdot R_{ij}) dq$$

In Figure 2 are plotted as circles values of  $Z = x_1(Z_{11} + Z_{12}) + x_2(Z_{22} + Z_{21})$  which is the mean coordination number and corresponds to twice the total number of nearest neighbour pairs per particle.  $Z$  was calculated for different values of  $1 \leq \sigma_2/\sigma_1 \leq 1.442$  and we observed that its variation with composition and size difference for a given packing fraction is very precisely given by

$$Z = Z^0 - ax_1 \Phi_2 (V_2^0 - V_1^0)/V_1^0 \tag{8}$$

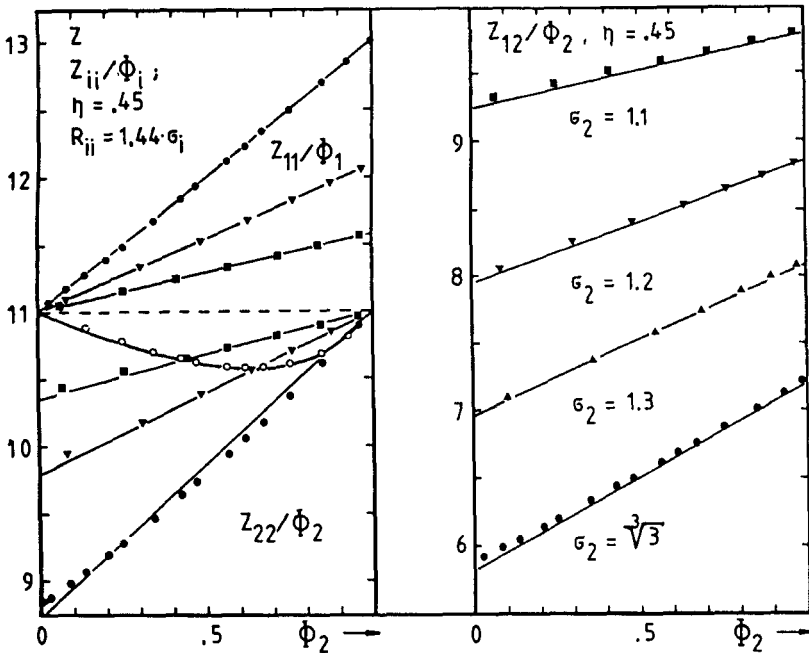


Figure 2 Left: Mean coordination number  $Z$  obtained from Eq. (7) (circles) and from Eq. (8) (full line) for  $\eta = 0.45$  and  $\sigma_2/\sigma_1 = 1.442$ . Relative partial coordination number  $Z_{11}/\Phi_1$  (upper part) and  $Z_{22}/\Phi_2$  (lower part) obtained from Eq. (7) (●:  $\sigma_2/\sigma_1 = 1.442$ ; ▼:  $\sigma_2/\sigma_1 = 1.2$ ; ■:  $\sigma_2/\sigma_1 = 1.1$ ) and from Eq. (9) (full lines).  $\eta$  was 0.45. Right: Relative partial coordination numbers  $Z_{12}/\Phi_2$  obtained from Eq. (7) (●:  $\sigma_1/\sigma_2 = 1.442$ ; ▲:  $\sigma_2/\sigma_1 = 1.3$ ; ▼:  $\sigma_2/\sigma_1 = 1.2$ ; ■:  $\sigma_2/\sigma_1 = 1.1$ ) and from Eq. (10) (full lines).  $\eta$  was 0.45.

$Z^0$  is the coordination number of the pure components.  $Z^0 = 11.00$  and  $a = 0.53$  for  $\eta = 0.45$ . The maximum relative deviation between  $Z$  calculated using Eq. (7) and Eq. (8), respectively (circles and full drawn curve in Figure 2), was found to be smaller than 0.2%. The maximum relative deviation from  $Z^0$  amounts to about -4% and -1% for  $\sigma_2/\sigma_1 = 1.442$  and 1.2, respectively.  $Z = Z^0$  will be a good approximation for not too large size difference.

The points  $Z_{ii}/\Phi_i$  calculated from Eq. (7) and given in Figure 2 for three different  $\sigma_2/\sigma_1$  values are seen to vary close to linear with  $\Phi_i$ . The deviation from linearity is strongest for  $Z_{22}/\Phi_2$  at small  $x_2$  and large  $\sigma_2/\sigma_1$ . The coordination numbers divided by the volume fractions may be written:

$$\begin{aligned} Z_{11}/\Phi_1 &= Z^0 + b_1 \cdot \Phi_2 \cdot (1 - \sigma_1/\sigma_2) \\ Z_{22}/\Phi_2 &= Z^0 - b_2 \cdot \Phi_1 \cdot (1 - \sigma_1/\sigma_2) \end{aligned} \quad (9)$$

For  $\eta = 0.45$  we obtained  $Z^0 = 11.0$ ,  $b_1 = 6.5$  and  $b_2 = 7.4$ . For the composition range investigated which was  $0.999 \geq x_i \geq 0.001$  the maximum relative deviation between Eqs (7) and (9) (points and full drawn curves) is largest for  $Z_{22}/\Phi_2$  at  $x_2 = 0$  where it amounts to less than 1%. It is much smaller for  $Z_{11}/\Phi_1$ . For  $\sigma_2/\sigma_1 = 1.442$   $Z_{ii}/\Phi_i$  changes by about 20% on varying  $\Phi_i$  from 1 to 0. For most alloy systems the size effect will be smaller and frequently  $Z_{ii} = \Phi_i Z^0$  might be a sufficiently accurate approximation. It seems interesting to note that one obtains a relation of this type for a hypothetical system in which the atoms are completely disordered beyond the HS-diameters  $\sigma_i$ , i.e. for which  $\rho_{ii}(r > \sigma_i) = x_i \cdot N/V = x_i \cdot \rho_0$ , namely  $Z_{ii}/\Phi_i = 8\eta[(R_{ii}/\sigma_i)^3 - 1]$ , independent from composition and the special choice of  $R_{ii}$ . The variation of  $Z_{ii}/\Phi_i$  with  $\Phi_i$  is due to the special form of  $\rho_{ii}(r)$  and, in fact,  $b_i$  in Eq. (9) and even the sign of  $b_i$  depends on the choice of  $R_{ij}$  as will be shown later.

For substitutional alloys one has  $Z_{ii}/x_i Z^0 = 1$ . The same quantity derived from Eq. (9), and calculated for the limiting case  $x_i \rightarrow 0$ , which corresponds to the maximum deviation, becomes  $Z_{ii}/x_i Z^0 = (\sigma_i/\sigma_j)^3 (1 \pm b_i (1 - \sigma_1/\sigma_2)/Z^0)$  yielding 0.4 and 2.4 for the small ( $\sigma_1 = 1$ ) and the large ( $\sigma_2 = 1.442$ ) spheres, respectively. For only 10% size difference one still obtains -20 and +25% deviation from the value of substitutional alloys.

Inserting Eqs (8) and (9) into  $Z = x_1 Z_{11} + x_2 Z_{22} + 2x_1 Z_{12}$  yields

$$\begin{aligned} Z_{12}/\Phi_2 &= \frac{1}{2} Z^0 (1 + V_1^0/V_2^0) - \frac{1}{2} a (V_2^0/V_1^0 - 1) \\ &\quad - \frac{1}{2} \Phi_1 (b_1 - b_2 x_2/x_1) \cdot (1 - \sigma_1/\sigma_2) \end{aligned} \quad (10)$$

$Z_{21}$  may be obtained from  $Z_{21}/\Phi_1 = (Z_{12}/\Phi_2) \cdot (V_2^0/V_1^0)$ . Plots according to Eq. (10) are given in Figure 2 as full drawn curves and are compared with individual points obtained from Eq. (7). For the  $\sigma_2/\sigma_1$ -range investigated the deviation is less than 1%.

We will now discuss the magnitude of the three terms on the right hand side of Eq. (10). For  $\sigma_2/\sigma_1 = 1.442$ , the first two terms are equal to 7.33 and  $-0.53$ , respectively. The third term vanishes for  $b_1x_1 = b_2x_2$  and is equal to  $-1.00$  and  $+0.38$  for  $x_1 = 1$  and  $x_1 = 0$ , respectively. For only ten percent size difference the corresponding numbers in the same order are 9.63,  $-0.09$ ,  $-0.29$  and 0.25. This demonstrates that for small size differences  $Z_{12} = \frac{1}{2}Z^0(1 + V_1^0/V_2^0) \cdot \Phi_2$  might be a sufficiently accurate approximation. Composition independent  $Z_{12}/\Phi_2$  is also obtained for the above mentioned case  $\rho_{ij}(r > \sigma_i) = x_j \cdot \rho_0$  which yields  $Z_{ij}/\Phi_j = Z^0(1 + \sigma_i/\sigma_j)^3/8$ .

For substitutional alloys  $Z_{ij}/(x_jZ) = 1$ . In the present case we find values of 0.65 and 1.57 for  $x_1 = 0$  and 1, respectively, and inserting 1.44 for  $\sigma_2/\sigma_1$ . With only 10% size difference we still obtain maximum deviations of 11%. One sees that the Warren-Cowley SRO Parameter  $\alpha = 1 - Z_{ij}/(x_jZ)$  loses its meaning if the size difference becomes too important.

The Eqs (8) and (9) are approximately valid in the whole  $\eta$ -range of dense liquids.  $Z_{22}/\Phi_2$  becomes stronger curved for larger  $\eta$ . With decreasing  $\eta$ , the difference between  $b_1$  and  $b_2$  becomes more pronounced. At  $\eta = 0.5$  these two quantities are almost identical.  $Z^0$ ,  $b_1$  and  $b_2$  increase monotonically with increasing  $\eta$ .  $a$  has a maximum value at about  $\eta = 0.43$ . The following empirical equations allow the calculation of the different coordination numbers

$$\begin{aligned} Z^0 &= 16.62 \cdot \eta + 13.75 \cdot \eta^2 + 60.99 \cdot \eta^3 - 117.2 \cdot \eta^4 \\ Z &= Z^0 - x_1\Phi_2(1.4\eta - 64.4\eta^8)(\sigma_2^3 - \sigma_1^3)/\sigma_1^3 \\ Z_{11} &= \Phi_1Z^0 + \Phi_1\Phi_2 \cdot 135\eta^{3.8}(\sigma_2 - \sigma_1)/\sigma_2 \\ Z_{22} &= \Phi_2Z^0 - \Phi_1\Phi_2 \cdot 68\eta^{2.8}(\sigma_2 - \sigma_1)/\sigma_2 \\ Z_{12} &= (Z - x_1Z_{11} - x_2Z_{22})/(2 \cdot x_1) \end{aligned} \tag{11}$$

$R_{ij}$  was always  $0.72 \cdot (\sigma_i + \sigma_j)$ . In the range  $0.2 \leq \eta \leq 0.5$  and  $\sigma_2/\sigma_1 \leq 1.442$  the results deviate by more than 1% from Eq. (6) only for  $Z_{22}/\Phi_2$  and  $Z_{12}/\Phi_2$  if simultaneously  $\eta$  is large and  $x_2$  is small.

We also studied the influence of  $R_{ij}$ . For  $\eta = 0.45$  and  $R_{ij}/(\sigma_i + \sigma_j) = 0.55$  and 0.65 we observed the same qualitative behaviour as described by Eqs (8) and (9). With the results obtained for 0.65 given in parenthesis, the values of  $Z^0$ ,  $a$ ,  $b_1$  and  $b_2$  are: 3.85 (8.8), 0.30 (0.5),  $-1.0$  (2.6) and  $-1.0$  (4.2), respectively. The sign of the slope of the  $Z_{ii}/\Phi_i$



versus  $\Phi_i$  curves has changed for  $R_{ij}/(\sigma_i + \sigma_j) = 0.55$  with respect to the other cases investigated.

### 3 INTERACTION TERM OF THE FLORY-HUGGINS EQUATION AND GENERAL CONCLUSIONS

We postulate composition independent interactions  $w_{ij}$  between the nearest neighbour pairs defined according to Eq. (6). The enthalpy of mixing per particles is then obtained by inserting into Eq. (1) the  $Z^0$  and  $Z_{ij}$  values of Eqs (8) to (10) or of the Eq. (11):

$$\begin{aligned} \Delta H = & -x_1\Phi_2Z^0[w_{12} - \frac{1}{2}w_{11} - \frac{1}{2}w_{22} + \frac{1}{2}(1 - V_1^0/V_2^0)(w_{22} - w_{12})] \\ & - \frac{1}{2}\Phi_1\Phi_2[x_1b_1w_{11} + x_2b_2w_{22} - (x_1b_1 + x_2b_2)w_{12}]\Delta\sigma/\sigma_2 \\ & + \frac{1}{2}x_1\Phi_2a \cdot w_{12}\Delta V/V_1^0 \end{aligned} \quad (12)$$

The first line contains the first terms on the righthand side of Eqs (8) to (10) which were shown to be good first approximations for not too large size difference. Inserting  $w$  for  $w_{12} - w_{11}/2 - w_{22}/2$  this first line becomes:

$$\begin{aligned} \Delta H_1 = & -x_1\Phi_2Z^0[w + (1 - V_1^0/V_2^0)(w_{22} - w_{12})] \\ = & -x_2\Phi_1Z^0[w + (1 - V_2^0/V_1^0)(w_{11} - w_{12})] \end{aligned} \quad (13)$$

The terms in brackets are independent from composition and  $\Delta H_1$  should correspond to the interaction term  $-x_1\Phi_2w_{FH}$  of the Flory-Huggins Eq. (4). For  $w_{FH}$  two different values are obtained depending on the choice of indexing the particles. Equation (13) gives a satisfactory explanation of this fact.

For substitutional alloys we have  $V_1^0 = V_2^0$ , the coefficients  $a$ ,  $b_1$  and  $b_2$  vanish and Eq. (12) reduces to Eq. (2) as it should. For  $w_{11} = w_{22} = w_{12}$  only the first and the second line of Eq. (12) vanish and we are in trouble finding a finite enthalpy of mixing:  $\Delta H_3 = w_{12}ax_1\Phi_2\Delta V/(2V_1^0)$ . The reason is that the total number of nearest neighbour pairs is reduced if the packing fraction is kept constant on mixing the pure components.  $\Delta H_3$  vanishes if  $\eta$  is changed on mixing to  $\eta'$  such that  $Z^0(\eta') - a(\eta')x_1\Phi_2\Delta V/V_1^0 = Z^0(\eta)$ ; which yields a negative excess volume.

The relatively simple description of the mean and the partial coordination numbers which is presented in this paper seems to be useful for better understanding the structure of disordered systems consisting of unequal hard spheres, and it offers perhaps a chance finding a formalism which allows to describe chemical order in this complex case. We doubt however that our partial coordination numbers are of immediate

use for discussing metallic systems. No doubt that the most important part of the ordering enthalpy, Eq. (3), may be attributed to nearest neighbour interactions.<sup>9</sup> But this interaction is certainly not proportional to the partial coordination numbers discussed in this paper. It depends on the special shape of the ordering potentials, which themselves correspond to a very simplified modelling of the much more complex "reality" deduced from fundamental theories.<sup>2</sup> It seems plausible that the "density at contact"<sup>2</sup> or the number of neighbours in a given distance interval beyond  $\sigma_i$  (not proportional to  $\sigma_i + \sigma_j$ ) are the quantities to be chosen for calculating  $\Delta H_{\text{ord}}$ . Once it is clear which quantities are needed, the corresponding analytical expressions for their evaluation may be obtained in the same way as for the partial coordination numbers discussed in this paper.

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