

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

Meaning of the concentration independent partial interference functions of liquid binary systems

V. I. Korsunsky^a; Yu. I. Naberukhin^a

^a Institute of Chemical Kinetics and Combustion, Academy of Science, Novosibirsk, USSR

To cite this Article Korsunsky, V. I. and Naberukhin, Yu. I.(1976) 'Meaning of the concentration independent partial interference functions of liquid binary systems', *Physics and Chemistry of Liquids*, 5: 2, 137 – 149

To link to this Article: DOI: 10.1080/00319107608084114

URL: <http://dx.doi.org/10.1080/00319107608084114>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Meaning of the Concentration Independent Partial Interference Functions of Liquid Binary Systems

V. I. KORSUNSKY and YU. I. NABERUKHIN

Institute of Chemical Kinetics and Combustion, Academy of Sciences, Novosibirsk 630090, USSR.

(Received August 22, 1975)

The procedure of obtaining the concentration independent partial interference functions $I_{ij}(k)$ which was applied in many articles for the analysis of diffraction experiments on liquid metal alloys is reproduced for the model system of hard spheres. As in the real alloys the functions $I_{ij}(k)$ allow one to reconstruct the total interference functions of the system in the wide range of compositions. However, $I_{ij}(k)$ differ in an essential way from the true partial functions $I_{ij}(k)$ of the model system. Thus, although for every real binary alloy it is possible to find (in a variety of ways) the concentration independent functions $I_{ij}(k)$, they have no clear physical interpretation and, in any case, do not represent the true partial interference functions of the system.

1 INTRODUCTION

The extraction of structural information from diffraction patterns of binary solutions is difficult enough even in the case of simple atomic liquids. The reason is that the coherent scattering of the radiation (X-rays, neutrons, etc.) is characterized in such systems by three structure-sensitive functions—partial structure factors S_{11} , S_{22} , S_{12} , in contrast with one-component systems where a single structure factor is needed. With the help of these functions the intensity of the scattered radiation at an angle 2δ is expressed as^{1,2}

$$I(k) = x_1 f_1^2(k) S_{11}(k) + x_2 f_2^2(k) S_{22}(k) + 2(x_1 x_2)^{1/2} f_1(k) f_2(k) S_{12}(k). \quad (1)$$

The partial structure factors are related to the partial radial distribution functions by

$$S_{ij}(k) = \delta_{ij} + \frac{4\pi}{k} (\rho_i \rho_j)^{1/2} \int [g_{ij}(r) - 1] r \sin kr \, dr. \quad (2)$$

Here ρ_i is the average number density of i th species ($i = 1, 2$), $k = 4\pi \sin \theta / \lambda$, λ – the wavelength of radiation, $f_i(k)$ – the atomic coherent scattering amplitudes, $x_i = \rho_i / (\rho_1 + \rho_2)$, δ_{ij} – the Kronecker symbol. One often introduces in practice the so-called total interference function defined as (see, for example, Wagner and Halder³)

$$I(k) = \frac{I(k) - x_1 x_2 (f_1 - f_2)^2}{\langle f \rangle^2}. \quad (3)$$

This function is, by analogy with (1), the linear combination of the partial interference functions $I_{ij}(k)$:

$$I(k) = W_{11} I_{11}(k) + W_{22} I_{22}(k) + 2W_{12} I_{12}(k), \quad (4)$$

where

$$W_{ij} = \langle f \rangle^{-2} x_i x_j f_i f_j, \quad (i, j = 1, 2) \quad (5)$$

$$\langle f \rangle = (x_1 f_1 + x_2 f_2) \quad (6)$$

and

$$I_{ij}(k) = 1 + \frac{4\pi}{k} (\rho_1 + \rho_2) \int [g_{ij}(r) - 1] r \sin kr \, dr. \quad (7)$$

It is easy to see from (2) and (7) that the partial functions I_{ij} and S_{ij} are connected by the relations

$$I_{ii}(k) = 1 + \frac{1}{x_i} [S_{ii}(k) - 1] \quad (i = 1, 2) \quad (8)$$

$$I_{12}(k) = 1 + (x_1 x_2)^{-1/2} S_{12}(k). \quad (9)$$

From these formulae it follows that in order to determine three partial functions one needs, in principle, three independent diffraction patterns for each solution. One of them may be obtained, for example, from the scattering of X-rays, and two others, as was suggested by Keating,⁴ from neutron diffraction experiments with different isotopes. This method is, in principle, quite rigorous, but requires much labour. There have been only two attempts to realize it for liquid alloys; Cu_6Sn_5 ⁵ and Cu-Te ⁶. Here three neutron diffraction experiments was used with isotope enrichment of Cu. Already these studies reveal considerable difficulties of this procedure. Because of small differences between the scattering amplitudes f_i of the isotopes, particularly, between ^{63}Cu , ^{65}Cu and natural Cu which were used, the calculated $I_{ij}(k)$ showed large fluctuations.^{5,6} Besides, for many systems it is difficult or impossible to find suitable isotopes for realizing the Keating procedure.

All these difficulties stimulated search for less rigorous but simpler and

more accessible methods for the determination of partial functions. With that end in view Halder and Wagner⁷ proposed a method which is based on the assumption that the partial interference functions $I_{ij}(k)$ are independent of concentration over a wide range of alloy compositions. This method does not require several kinds of radiation and the isotopic substitution experiments. It is enough, in principle, to measure the scattering intensity from three alloys of different concentrations and then to solve the set of three Equations (4) to determine the three functions $I_{ij}(k)$. The concentration independent partial interference functions obtained in such a manner will be denoted by \bar{I}_{ij} , to distinguish them from the true partial functions I_{ij} . It is possible now to calculate the total interference functions of alloy at other concentrations on the basis of $\bar{I}_{ij}(k)$. Good agreement between such a reconstruction and the experimental curves is considered as the justification of the initial assumption about the concentration independence of $\bar{I}_{ij}(k)$.

The method described above was used by several authors to evaluate the partial functions for various alloys: Ag-Sn,⁷ Au-Sn,⁸ Cu-Sn,⁹ Cu-Mg,¹⁰ Cu-Ag,¹¹ Mg-Ag,¹² Mg-Sn,¹³ Cu-Sb,¹⁴ Na, K, and Al-Mg,^{15,16} Hg-In and Hg-Tl.¹⁷ In all cases the concentration independent partial functions \bar{I}_{ij} thereby obtained allowed the reconstruction of the total interference functions of the alloys over practically the whole range of compositions. So impressive a success of the quite arbitrary, on the face of it, procedure is a nontrivial fact. It may seem that, indeed, an effective method for the determination of the partial functions I_{ij} has been discovered. However, the only criterion that these functions are correct is essentially the good results of the reconstruction of the experimentally measured $I(k)$. This criterion, as was mentioned by the authors of the original proposal,⁷ is a necessary but not sufficient condition for the correctness of the initial assumption. But subsequent articles both by these and other authors demonstrated only the existence of the concentration independent partial functions \bar{I}_{ij} , but did not answer the question whether the \bar{I}_{ij} 's thereby obtained actually represent the true partial interference functions I_{ij} of the alloys.

In order to answer this question we reproduce in the present work the procedure of obtaining the concentration independent partial interference functions for a model system: a binary mixture of hard spheres of different diameters. The use of the model system allows us to elucidate the physical significance of the method discussed above since for this model, in contrast with real alloys, there exists an analytical solution for the partial functions S_{ij} on the basis of the Percus-Yevick equation.^{1,2} The results of our calculations show that the concentration independent functions \bar{S}_{ij} and \bar{I}_{ij} bear no resemblance to the true partial functions S_{ij} and I_{ij} (this is clear even from the fact that the latter are quite significantly dependent on the composition of a mixture). Nevertheless, the total interference functions (or

the scattered intensities) which were reconstructed on the basis of the functions \tilde{I}_{ij} and \tilde{S}_{ij} are found to be very close to the true ones in the wide region of compositions. It follows from this that the possibility of reconstruction of the experimental functions $I(k)$ does not provide a useful criterion of the correctness of the Halder–Wagner procedure. Therefore one cannot ascribe any direct physical significance to the functions $\tilde{I}_{ij}(k)$ which were obtained in the various works cited above.

2 RESULTS OF THE CALCULATIONS

Since all the authors used the experimental data on X-ray scattering to obtain the concentration independent partial interference functions $\tilde{I}_{ij}(k)$ we shall also simulate this case. The partial structure factors $S_{ij}(k)$ were calculated with the help of the formulae of the article¹ (after correction of numerous misprints). For the calculation of intensities and interference functions one must choose the atomic scattering amplitudes of the components. This point is not of great importance for our problem. Therefore, more or less arbitrarily, we choose the atomic scattering factors of the atoms Cu and In as f_1 and f_2 , respectively.¹⁸ The structure factors of these liquid metals are well described by the hard sphere model with a packing density $\eta = 0.45$.^{11,19,20} Then it is possible to obtain diameters of the spheres σ from the formula $\eta = (\pi/6) \rho \sigma^3$ (ρ is the number density), viz. $\sigma_1 = \sigma_{\text{Cu}} = 2.2 \text{ \AA}$, $\sigma_2 = \sigma_{\text{In}} = 2.86 \text{ \AA}$ and $\alpha = \sigma_1/\sigma_2 = 0.77$. The main calculations were made with the above parameters of the system of hard spheres. The partial and total interference functions were calculated for the values of x_2 (the fraction of large spheres) 0; 0.15; 0.25; 0.35; 0.50; 0.65; 0.75; and 1.0. The three concentration independent functions $\tilde{I}_{11}(k)$, $\tilde{I}_{22}(k)$ and $\tilde{I}_{12}(k)$ were obtained by solving the three Equations (4) on the basis of the calculated curves $I(k)$ for $x_2 = 0.15; 0.35; 0.65$.

From Figure 1 it is seen that the true partial interference functions $I_{ij}(i)$ depend considerably on concentration. This concerns particularly $I_{11}(k)$ the first peak of which moves from 3.1 \AA^{-1} at $x_2 = 0$ to 2.7 \AA^{-1} at $x_2 = 0.75$, the height of the peak being diminished by a factor of 1.56. Figure 2 shows that the functions $\tilde{I}_{11}(k)$ and $I_{11}(k)$ ($x_2 = 0.25$) are very different: although the first peak positions are displaced only by 0.1 \AA^{-1} the values of the functions at the maximum differ by a factor of 1.5. The first peak of $\tilde{I}_{22}(k)$ is considerably narrower and is displaced by 0.2 \AA^{-1} relative to the first peak of $I_{22}(k)$. Furthermore, the functions $\tilde{I}_{11}(k)$ and $\tilde{I}_{22}(k)$ have additional oscillations on the left and right side, respectively, of the main peak which are absent in the curves of the true $I_{11}(k)$ and $I_{22}(k)$. In the small k region the functions $\tilde{I}_{11}(k)$ and $\tilde{I}_{22}(k)$ coincide practically with the interference functions of the corresponding pure components, but differ con

siderably from the partial functions in solutions which strongly deviate from zero in this region (Figures 1 and 2).

It is interesting to note that the concentration independent $\bar{I}_{11}(k)$ and $\bar{I}_{22}(k)$ resemble in general the interference functions of the pure components rather than the true $I_{ij}(k)$ in the alloys (Figure 2). Such a resemblance was observed practically in all the works where the functions $\bar{I}_{ij}(k)$ were obtained from the experimental data. It was even shown by Waseda and coworkers¹⁵⁻¹⁷ that for some alloys (Hg-Tl, Hg-In, K-Na, Mg-Al) it is quite possible to accept the interference functions of the pure components as $\bar{I}_{11}(k)$ and $\bar{I}_{22}(k)$ and to obtain $\bar{I}_{12}(k)$ in each alloy from the only one Equation (4). The $\bar{I}_{12}(k)$ thereby obtained did not differ practically from that which was found by solving the three Equations (4) for three alloys. To all appearances, the close resemblance of $\bar{I}_{11}(k)$ and $\bar{I}_{22}(k)$ with $I(k)$'s of the pure components is a general property of the procedure which assumes the partial functions to be independent of concentration.

Thus, the concentration independent partial functions $\bar{I}_{ij}(k)$ are very different from the true functions $I_{ij}(k)$ for the model system of hard spheres. Nevertheless, these functions $\bar{I}_{ij}(k)$ allow one to reconstruct with good accuracy the true total $I(k)$, at concentrations differing from those which were used for the calculations of $\bar{I}_{ij}(k)$. Figure 3 demonstrates this fact. The maximum differences are observed in the region of the main peak: 2.1% at $k = 2.8 \text{ \AA}^{-1}$ ($x_2 = 0.25$); 3% at $k = 2.8 \text{ \AA}^{-1}$ ($x_2 = 0.5$); 3.4% at $k = 2.5 \text{ \AA}^{-1}$ ($x_2 = 0.75$). At larger k the true curve differs from the reconstruction not more than by one per cent. Therefore, the calculation of the model system reproduces the main result of the works⁹⁻¹⁷ in which the total interference functions reconstructed on the basis of $\bar{I}_{ij}(k)$ did not differ from the experimental ones within the errors of the experiment (some per cents)†. Since the functions $\bar{I}_{ij}(k)$ are not the true partial functions in the model system, the same statement is valid with great probability concerning the concentration independent functions $\bar{I}_{ij}(k)$ which were obtained for the real alloys.⁷⁻¹⁷

Moreover, the procedure of obtaining the functions $\bar{I}_{ij}(k)$ has in itself essential defect. Since it is necessary to achieve only approximate reconstruction of the total $I(k)$'s one can find a wide variety of the functions \bar{I}_{ij} which ensure an acceptable result within an accuracy of 3-5 per cents determined by the errors of diffraction experiment. In other words, there is a basic uncertainty in the choice of the functions $\bar{I}_{ij}(k)$. In order to prove this statement we calculated the functions $\bar{I}_{ij}(k)$ from the various set of

† It will be noted that the reconstruction is not able to give good results if $x_2 \rightarrow 0$ or $x_2 \rightarrow 1$. The true total functions $I(k)$ approach under these conditions the interference functions of pure components, I_i , while the reconstructed functions $I(k)$ approach $\bar{I}_{ij}(k)$, I_i and \bar{I}_{ii} being considerably different (Figure 2).

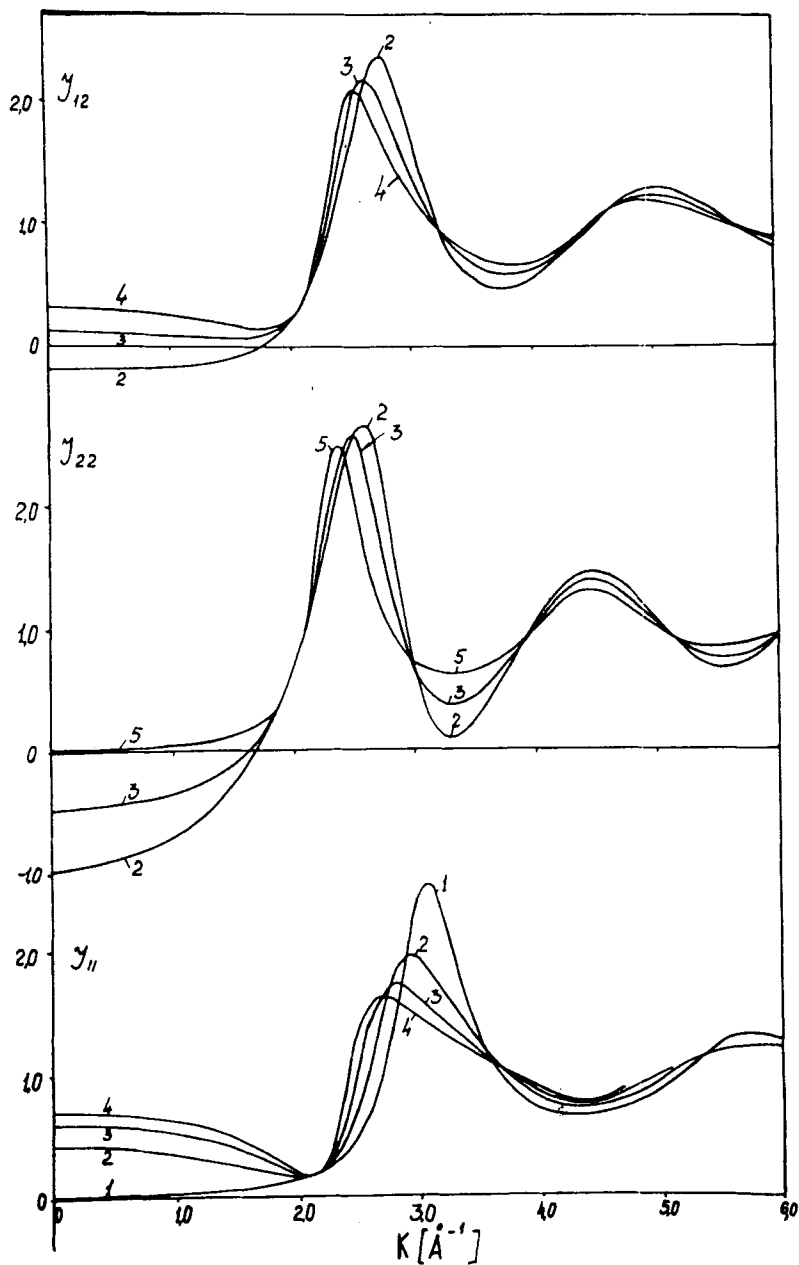


FIGURE 1 True partial interference functions $I_{ij}(k)$ for the binary mixture of hard spheres. $\alpha = 0.77$; $\eta = 0.45$; $\sigma_2 = 2.86 \text{ \AA}$ 1 - $x_2 = 0$; 2 - $x_2 = 0.25$; 3 - $x_2 = 0.50$; 4 - $x_2 = 0.75$; 5 - $x_2 = 1.0$.

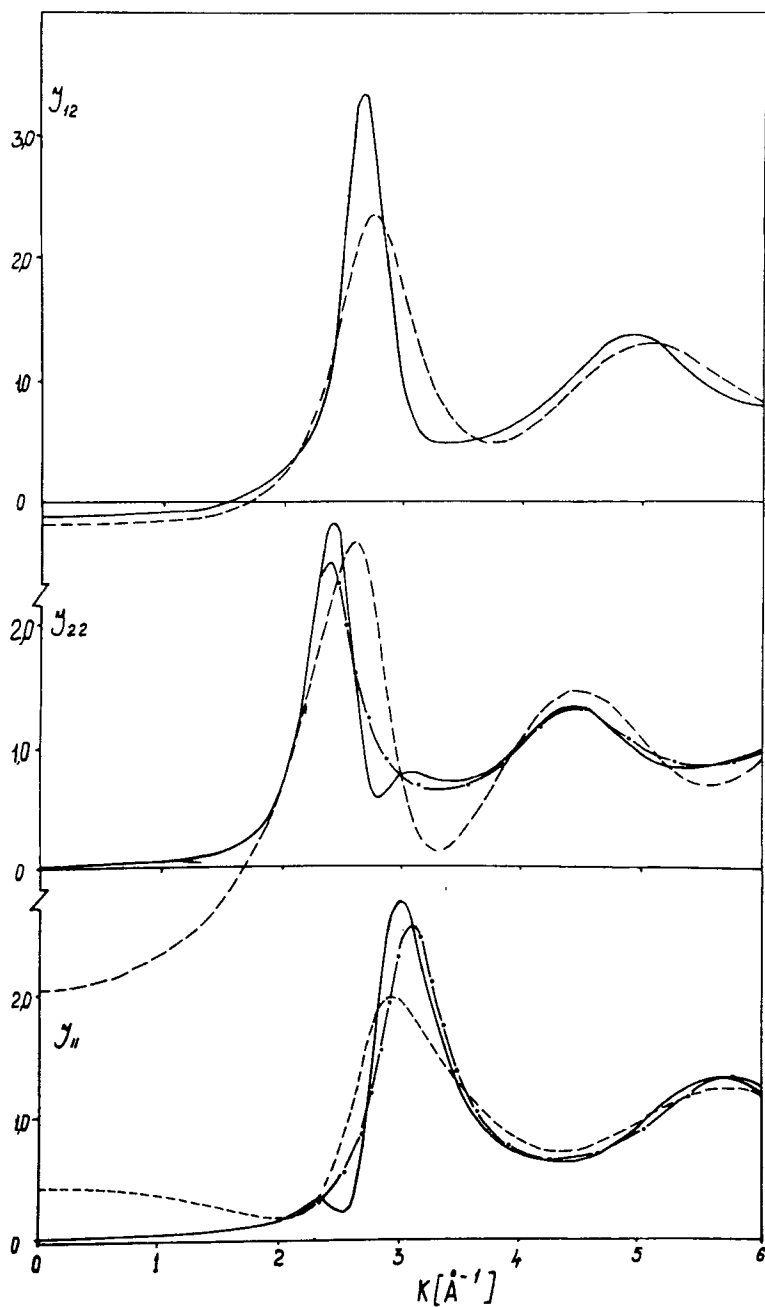


FIGURE 2 Comparison of I_{ij} with I_{ij} and I_i .
 — The concentration independent partial interference functions I_{ij} .
 ---- The true partial functions I_{ij} ($x_2 = 0.25$).
 - · - · The interference functions of pure components I_i .
 $\alpha = 0.77$; $\sigma_2 = 2.86 \text{ \AA}$.

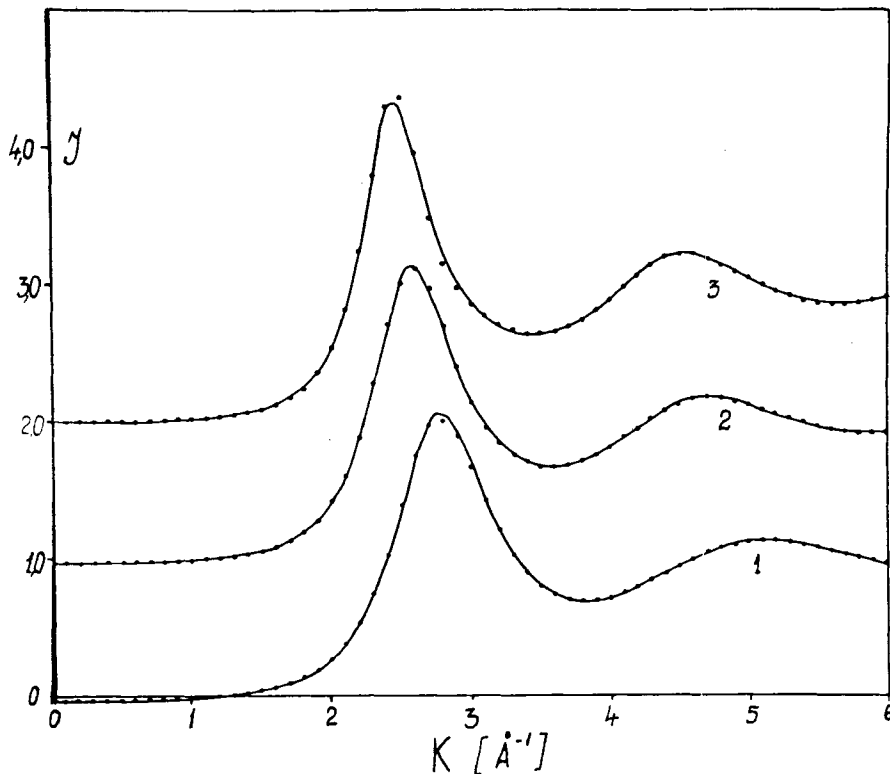


FIGURE 3 Reconstruction of the total interference functions $I(k)$ as a weighted sum of the concentration independent functions $I_{ij}(k)$. The true functions $I(k)$ are displayed by the solid lines and reconstruction - by the points. I_{ij} are calculated by means of Equation (4) from $I(k)$ at concentrations $x_2 = 0.15; 0.35; 0.65$.

three true curves $I(k)$. For greater clarity of the results, we decrease in this calculation the parameter α taking it equal to 0.5 which corresponds to the diameter of large spheres $\sigma_2 = 4.4 \text{ \AA}$.

Figure 4 shows that the functions $\hat{I}_{ij}(k)$ depend essentially on concentrations which were chosen for their calculation. Two variants of the functions $\hat{I}_{11}(k)$ and $\hat{I}_{12}(k)$ distinguish the most strongly: their oscillations in the k interval from 2 to 4 \AA^{-1} are quite different. Of course, as in the calculations with $\alpha = 0.77$, two variants of the functions $\hat{I}_{ij}(k)$ are very different from the true partial functions $I_{ij}(k)$. Nevertheless, these two sets of $\hat{I}_{ij}(k)$ describe quite well the true interference functions $I(k)$ at concentrations differing from those utilized in the calculation of $\hat{I}_{ij}(k)$. It is evident from Figure 5 that only at $x_2 = 0.15$ is the reconstruction bad. At other concentrations, the error is several per cent. These results demonstrate an unexpected feature of the procedure of obtaining $\hat{I}_{ij}(k)$: a good description (i.e.

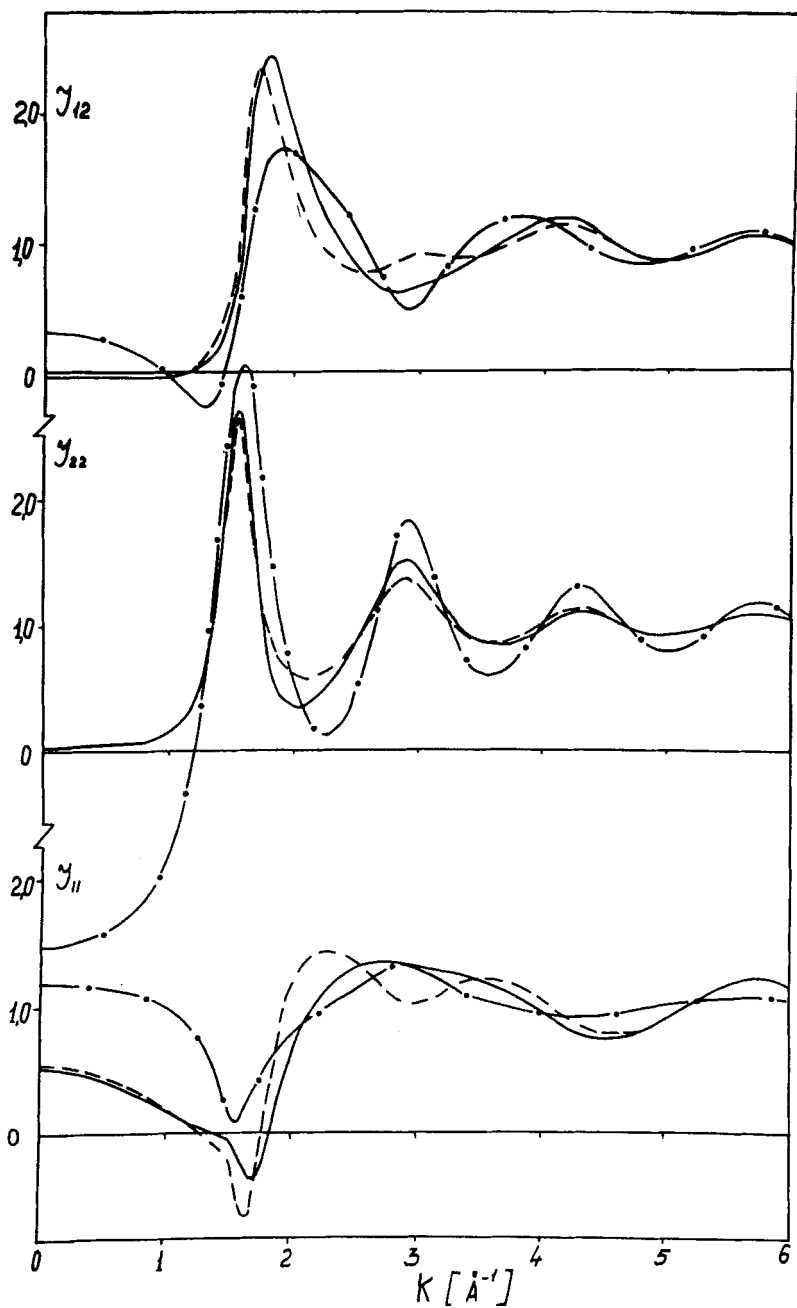


FIGURE 4 Comparison of the true and concentration independent partial functions.

$\alpha = 0.5$; $\eta = 45$; $\sigma_2 = 4.4 \text{ \AA}$.

--- The true $I_{ij}(k)$.

— The concentration independent functions $I_{ij}(k)$ calculated from $I(k)$ at $x_2 = 0.15; 0.35; 0.65$.

- · - The same, but calculated from $I(k)$ at $x_2 = 0.25; 0.5; 0.75$.

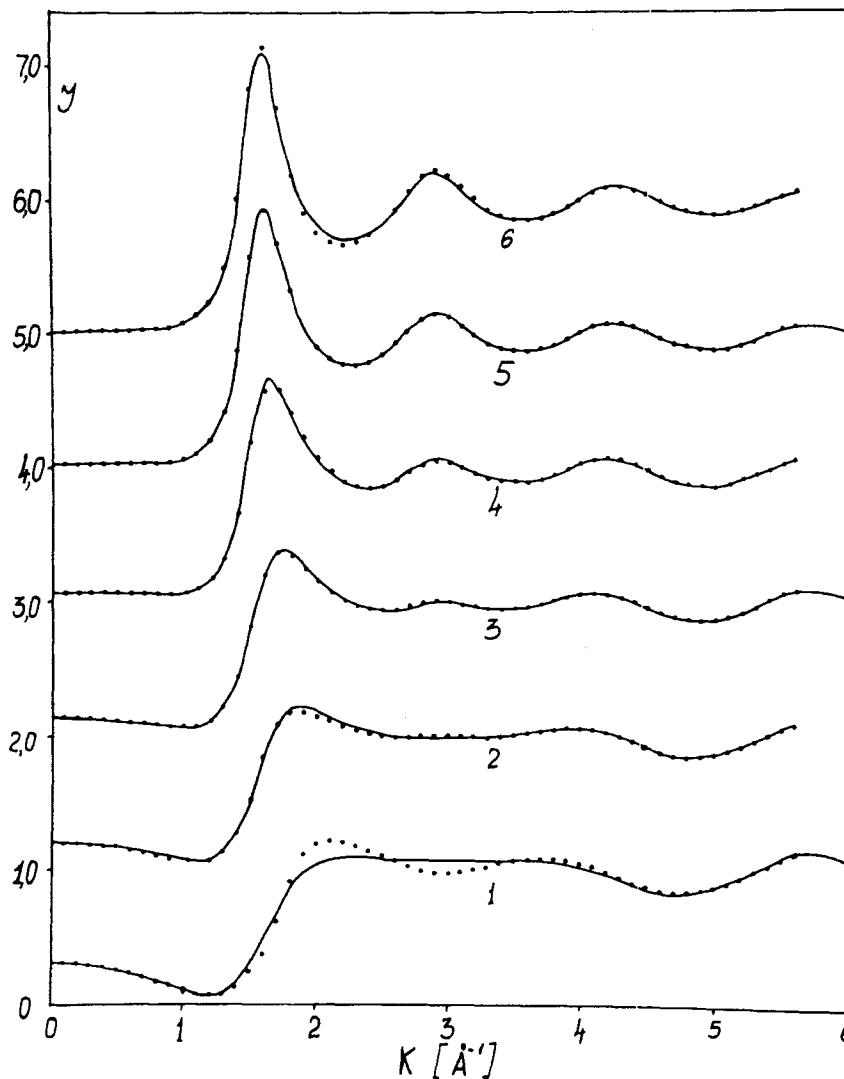


FIGURE 5 Reconstruction of the total interference functions $I(k)$ on the basis of the concentration independent functions $I_{ij}(k)$. The solid line represents the true functions $I(k)$ the points give the reconstruction.

$\alpha = 0.5$; $\eta = 0.45$; $\sigma_2 = 4.4 \text{ \AA}$. The curves 1, 3, 5 are reconstructed on the basis of the functions $I_{ij}(k)$ calculated from $I(k)$ at $x_2 = 0.25$; 0.5 ; 0.75 ; the curves 2, 4, 6 – on the basis of $I_{ij}(k)$ obtained at $x_2 = 0.15$; 0.35 ; 0.65 .

in the limits of the accuracy of diffraction experiment) of the intensity scattering gives a rather wide class of the three concentration independent functions $I_{11}(k)$, $I_{22}(k)$, $I_{12}(k)$, and not a unique set of these function, as was implied originally when developing the procedure.

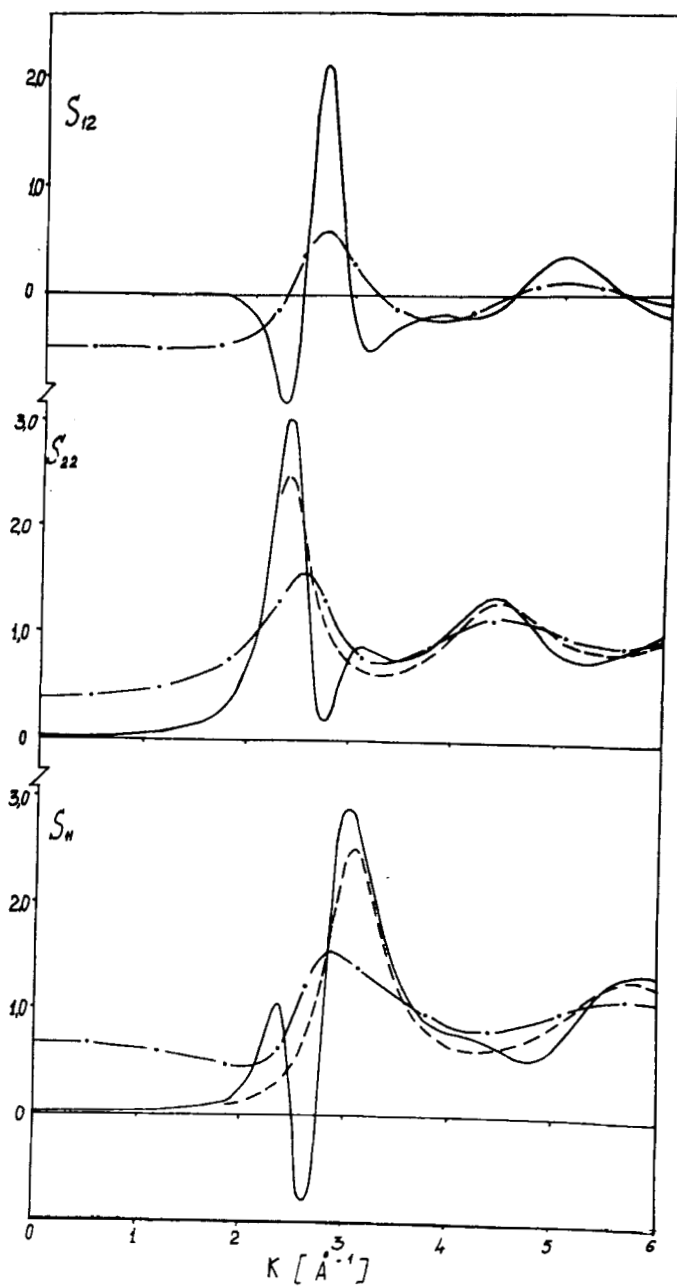


FIGURE 6 Partial structure factors $S_{ij}(k)$ for a binary mixture of hard spheres. $\alpha = 0.77$; $\eta = 0.45$; $\sigma_2 = 2.86 \text{ \AA}$.

— The concentration independent $S_{ij}(k)$.

- - - The true $S_{ij}(k)$.

· · · The structure factors of pure components $S_i(k)$.

Halder and Wagner⁷ supposed that the success of their procedure was based on the weak dependence of the true partial interference functions $I_{ij}(k)$ on composition of alloy, in contrast to the functions $S_{ij}(k)$ which, as it is well known, vary considerably with concentration.^{1,2} However, this point of view proved to be incorrect. By analogy with the method described above it is possible to determine the concentration independent partial structure factors $\hat{S}_{ij}(k)$ with the help of Equation (1). Figure 6 shows such functions calculated at $x_2 = 0.15; 0.35; 0.65$. They differ from the true partial functions even more than $\hat{I}_{ij}(k)$ †. Nevertheless, the functions $\hat{S}_{ij}(k)$ thereby obtained permit a good reconstruction of $I(k)$ at other concentrations ($x_2 = 0.25; 0.5; 0.75$). This result confirms once again that the success of any reconstruction of the total interference functions $I(k)$ on the basis of $\hat{I}_{ij}(k)$ in the real systems⁷⁻¹⁷ is hardly connected with the true concentration independence of the partial interference functions.

3 CONCLUSIONS

The extensive experimental data⁷⁻¹⁷ and our calculations for the model system of hard spheres show that for every binary solution it is always possible to find (moreover, in a variety of ways) three concentration independent functions $\hat{I}_{ij}(k)$ which allow one to reconstruct the total interference functions over a wide region of compositions with good accuracy. However this fact does not reveal any physical content in the functions $\hat{I}_{ij}(k)$ thus obtained, and reflects only mathematical properties of the equation sets (1) and (4) which allow a considerable freedom for the choice of $\hat{I}_{ij}(k)$ for a given accuracy of reconstruction. The calculations performed here show that the functions $\hat{I}_{ij}(k)$ differ considerably from the true partial interference functions which are, in principle, concentration dependent.

It is possible, of course, that specific systems or even a class of systems may exist in which the partial functions would depend only slightly on concentration in some interval of compositions. But the ability of the three concentration independent functions $\hat{I}_{ij}(k)$ to describe the observed intensity of scattering cannot be a criterion for such a situation. One needs here the more constructive arguments. Since the procedure of obtaining the functions $\hat{I}_{ij}(k)$ was carried out for all investigated systems⁷⁻¹⁷ in a purely formal way, it is highly probable that the functions $\hat{I}_{ij}(k)$ obtained in these works have no direct physical significance.

†It is of interest that $\hat{S}_{12}(k)$ becomes practically equal to zero if $k \rightarrow 0$ (Figure 6). Since $S_{12}(0) = (\langle N_1 N_2 \rangle - \langle N_1 \rangle \langle N_2 \rangle) / (\langle N_1 \rangle \langle N_2 \rangle)^{1/2}$ (see, for example Ashcroft and Langreth¹ this fact means that the requirement of the concentration independence of $S_{12}(k)$ automatically demands the fluctuations of the number of particles of different kind to be uncorrelated in solution.

References

1. Ashcroft, N. W. and Langreth, D. C., *Phys. Rev.* **156**, 685 (1967).
2. Enderby, J. E. and North, D. M., *Phys. Chem. Liquids* **1**, 1 (1968).
3. Wagner, C. N. J. and Halder, N. C., *Adv. Phys.* **16**, 241 (1967).
4. Keating, D. T., *J. Appl. Phys.* **34**, 923 (1963).
5. Enderby, J. E., North, D. M., and Egelstaff, P. A., *Phil. Mag.* **14**, 961 (1966).
6. Enderby, J. E., *J. de Phys.* **35**, C4-309 (1974).
7. Halder, N. C. and Wagner, C. N. J., *J. Chem. Phys.* **47**, 4385 (1967).
8. Wagner, C. N. J., Halder, N. C., and North, D. M., *Z. Naturforsch.* **24a**, 432 (1969).
9. North, D. M. and Wagner, C. N. J., *Phys. Chem. Liquids* **2**, 87 (1970).
10. Lukens, W. E. and Wagner, C. N. J., *Z. Naturf.* **28a**, 297 (1973).
11. Lukens, W. E. and Wagner, C. N. J., *Z. Naturf.* **30a**, 242 (1975).
12. Buhner, H. F. and Steeb, S., *Z. Naturf.* **24a**, 428 (1969).
13. Buhner, H. F. and Steeb, S., *Z. Naturf.* **25a**, 1862 (1970).
14. Knoll, W. and Steeb, S., *Phys. Chem. Liquids* **4**, 27 (1973).
15. Waseda, Y. and Ohtani, M., *Phys. Stat. Sol.* **b48**, K77 (1971).
16. Waseda, Y., Ohtani, M., and Suzuki, K., *Z. Naturf.* **28a**, 1002 (1973).
17. Waseda, Y., Kuroha, M., Suzuki, K., and Ohtani, M., *Phys. Stat. Sol.* **b52**, 571 (1972).
18. Cromer, T. and Waber, J. T., *Acta Cryst.* **18**, 104 (1965).
19. Ashcroft, N. W. and Lekner, J., *Phys. Rev.* **145**, 82 (1966).
20. Halder, N. C. and Wagner, C. N. J., *Z. Naturf.* **22a**, 1489 (1967).