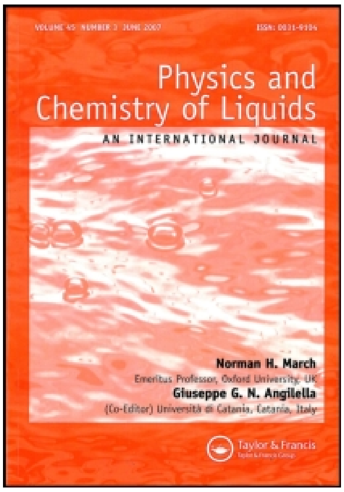

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Percus-Yevick Structure Factors for Liquid Alloys

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Percus–Yevick Structure Factors for Liquid Alloys

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Abstract—The partial structure factors $a_{ij}(i, j = 1, 2)$ for a binary mixture of hard spheres are evaluated in the Percus-Yevick approximation. They are shown to have a simple closed form and can be evaluated directly in terms of the assumed hard sphere diameters. As an example, the a_{ij} are evaluated for liquid Na K and are used to predict (i) the x-ray diffraction pattern and (ii) the isothermal compressibility. In both cases, the agreement with the experimental data is good.

1. Introduction

The recent progress in the theory of liquid metals has stressed the importance of the liquid structure factor, $a(K)$. It is natural to seek, as several authors have done, to apply this theoretical work to liquid binary alloys, but this is difficult because it involves more detailed knowledge of the structure than is at present available. In principle the three partial structure factors ($a_{ij}(K)$, $i, j = 1, 2$) required to specify the structure of a liquid binary alloy can be obtained by experiment (Keating, 1963) but this is by no means straightforward and so far results of limited accuracy are available only for liquid Cu_6Sn_5 (Enderby et al., 1966). On the theoretical side, attempts to elucidate a_{ij} (Faber and Ziman, 1965, Toombs, 1965) have been limited to rather specialized systems and to restricted regions of K-space.

Recently, Ashcroft and Lekner (1966) have demonstrated that for a pure liquid the known solution of the Percus-Yevick equation for

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hard spheres gives a simple closed form for $a(K)$ which depends only on the effective packing density of the liquid. The object of this present paper is to show that the same model can be used to obtain the three partial structure factors for a liquid binary alloy, and these also turn out to have a simple closed form†. Many immediate advantages of this procedure then become apparent:

(i) Ashcroft and Lekner found that the P.Y. $a(K)$ was reliable for K values around the first peak and could be used for calculations of the electrical resistivity. By analogy, we would expect $a_{ij}(K)$ to be reliable over a similar region so that a careful calculation of the resistivity for alloys of the sort suggested by Faber and Ziman would then be possible.

(ii) By obtaining $a_{ij}(K)$ rather than its Fourier transform $g_{ij}(r)$, some comparison with experiment is possible.

(iii) The concentration dependence of a_{ij} can be investigated and considerable insight gained into both the general problem of liquid alloy structure and the interpretation of the many x-ray experiments which have now been carried out on binary alloys.

2. Correlation functions and related quantities

Consider a specimen consisting of N_1 atoms of species 1 and N_2 atoms of species 2 irradiated by monochromatic radiation of wavelength λ, and let f_i $(i = 1, 2)$ represent the coherent scattering amplitudes. Then the intensity of the scattered radiation at an angle 2θ is proportional to (Fournet, 1958)

$$I = \langle \sum_i \sum_j f_i f_j \exp i\boldsymbol{K}(\boldsymbol{R}_i - \boldsymbol{R}_j) \rangle = NF(K) \tag{1}$$

where

$$K = |\boldsymbol{K}| = 4\pi \sin\theta/\lambda$$

$$F(K) = m_1 f_1^2 a_{11} + m_2 f_2^2 a_{22} + 2(m_1\, m_2)^{1/2} f_1 f_2 a_{12} \tag{2}$$

$$N = N_1 + N_2$$

and

$$m_i = \frac{N_i}{N_1 + N_2}.$$

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† After this work was completed, we learnt that Dr. Ashcroft and Dr. Langreth had independently reached the same conclusions.

The partial structure factors introduced in (2) are related to the radial distribution function $g_{ij}(\boldsymbol{r}, \boldsymbol{r}')$ between an i^{th} particle at $\boldsymbol{r}$ and a j^{th} particle at $\boldsymbol{r}'$ $(g_{ij}(\boldsymbol{r}, \boldsymbol{r}') = g_{ji}(\boldsymbol{r}', \boldsymbol{r}))$ by

$$a_{ij}(K) = \delta_{ij} + \frac{4\pi}{K} (\varrho_i\varrho_j)^{1/2} \int \{g_{ij}(r) - 1\}\, r \sin Kr\, dr \qquad (3)\dagger$$

since $g_{ij}(\boldsymbol{r}, \boldsymbol{r}')$ depends only on $|\boldsymbol{r} - \boldsymbol{r}'|$. Here ϱ_i is the number density defined by N_i/V where V is the volume of the specimen.

Let $h_{ij}(r) = g_{ij}(r) - 1$ represent the total correlation function. Then the generalized Ornstein-Zernike direct correlation function $c_{ij}(r)$ is given (Pearson and Rushbrooke, 1957) by an equation of the form

$$h_{ij}(r) = c_{ij}(r) + \sum_{l=1,2} \varrho_l \int c_{il}(|\boldsymbol{r} - \boldsymbol{r}'|)\, h_{lj}(\boldsymbol{r}')\, d\boldsymbol{r}'. \qquad (4)$$

It follows from the well known properties of the Fourier transform of a convolution that

$$h_{ij}(K) = c_{ij}(K) + \sum_{l=1,2} \varrho_l c_{il}(K)\, h_{lj}(K) \qquad (5)$$

where for instance,

$$c_{ij}(K) = \frac{4\pi}{K} \int c_{ij}(r)\, r \sin Kr\, dr. \qquad (6)$$

For a binary alloy (5) represents four equations, but since the P.Y. solution for hard spheres requires $c_{ij} = c_{ji}$ [see Eq. (9) below], only three have to be considered. The solutions for h_{ij} (from now on we shall show explicitly the K dependence only when any ambiquity can arise) are

$$h_{11} = [c_{11}(1 - \varrho_2 c_{22}) + \varrho_2 c_{12}^2]\, P^{-1}$$

$$h_{22} = [c_{22}(1 - \varrho_1 c_{11}) + \varrho_1 c_{12}^2]\, P^{-1}$$

$$h_{12} = h_{21} = c_{12} P^{-1} \qquad (7)$$

with

$$P = 1 - \varrho_1 c_{11} - \varrho_2 c_{22} + \varrho_1\varrho_2 c_{11} c_{22} - \varrho_1\varrho_2 c_{12}^2.$$

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† This definition of a_{ij} is somewhat different from that used by Enderby *et al.* (1966) and Faber and Ziman (1965). If $\bar{a}_{ij}$ represents the partial structure factors used by these workers then

$$a_{ii} = 1 + m_i(\bar{a}_{ii} - 1); \quad a_{12} = (m_1 m_2)^{1/2}\, (\bar{a}_{12} - 1)$$

3. The known solutions of the P.Y. equations for hard spheres

For a pure liquid consisting of hard spheres, the P-Y integral equation has been solved independently by Wertheim (1963) and Thiele (1963). As Ashcroft and Lekner show, both of these solutions yield, by elementary arguments, the same simple form for $a(K)$. The P-Y equation for a binary hard sphere liquid has also been considered by Lebowitz (1964). Lebowitz obtains the Laplace transforms of $rg_{ij}(r)$ exactly, and these have been inverted and evaluated numerically by Throop and Bearman (1965). However, contact between theory and experiment is most readily established in K space and so we return to an intermediate step in Lebowitz's argument in which the direct correlation functions are rigorously derived. These are as follows:

$$\begin{aligned} -c_{ii}(r) &= a_i + b_i r + dr^3 \qquad && r < R_i \\ &= 0 && r > R_i \end{aligned} \tag{8}$$

and

$$\begin{aligned} -c_{12}(r) = -c_{21}(r) &= a_1 \qquad && r < \lambda \\ &= a_1 + [b(r-\lambda)^2 + 4\lambda\, d(r-\lambda)^3 + d(r-\lambda)^4]/r \\ & && \lambda < r < R_{12} \\ &= 0 && r > R_{12} \end{aligned} \tag{9}$$

The coefficients a, b, etc. depend only on the hard sphere diameters R_i, the number density, ϱ_i and the "volume density", ξ, given by

$$\begin{aligned} \xi &= \pi\varrho_1 R_1^3/6 + \pi\varrho_2 R_2^3/6 \\ &= \eta_1 R_1^3 + \eta_2 R_2^3. \end{aligned} \tag{10}$$

Lebowitz gives explicit expressions for a, b etc. and for convenience we repeat these here

$$\begin{aligned} a_i &= \frac{1}{k_B T}\ \frac{\partial p}{\partial \varrho_i} \\ b_1 &= -6[\eta_1 R_1^2 g_{11}^2(R_1) + \eta_2 R_{12}^2 g_{12}^2(R_{12})] \\ b &= -6[\eta_1 R_1 g_{11}(R_1) + \eta_2 R_2 g_{22}(R_2)]\, R_{12} g_{12}(R_{12}) \\ d &= \frac{1}{2}[\eta_1 a_1 + \eta_2 a_2] \end{aligned} \tag{11}$$

$$p = k_BT\left\{(\varrho_1 + \varrho_2)\,[1 + \xi + \xi^2] - \frac{18}{\pi}\eta_1\eta_2(R_2 - R_1)^2\,[(R_1 + R_2) + R_1R_2(\eta_1R_1^2 + \eta_2R_2^2)]\right\}(1 - \xi)^{-3}$$

$$g_{11}(R_1) = \left\{\left[1 + \frac{1}{2}\xi\right] + \frac{3}{2}\eta_2R_2^2(R_1 - R_2)\right\}(1 - \xi)^{-2}$$

$$g_{12}(R_{12}) = [R_2g_{11}(R_1) + R_1g_{22}(R_2)]/2R_{12}$$

$$R_{12} = \frac{R_1 + R_2}{2}; \quad \lambda = \frac{R_2 - R_1}{2}$$

and b_2 and g_{22} are obtained by replacing η_1 and R_1 by η_2 and R_2.

4. Derivation of a_{ij}

It is necessary to evaluate the three-dimensional Fourier transforms of (8) and (9) to yield $c_{ij}(K)$. This can be done immediately with the result

$$c_{ii}(K) = -\frac{4\pi}{K^2}\,[A_i \sin K_iR_i + B_i \cos K_iR_i + C_i]$$

$$c_{12}(K) = -\frac{4\pi}{K^2}\,[A \sin K\,R_{12} + B \cos KR_{12} + C \sin K\lambda + D \cos K\lambda] \tag{12}$$

where

$$A_i = [\alpha_i - \beta R_i/K^2]\,K^{-1}$$

$$B_i = [\gamma_i - \beta/K^2]\,K^{-2} - \delta_i$$

$$C_i = [\beta/K^2 - \varepsilon_i]\,K^{-2}$$

$$A = [\alpha - \beta R_{12}/K^2]\,K^{-1} \tag{13}$$

$$B = [\gamma - \beta/K^2]\,K^{-2} - \delta$$

$$C = \beta\lambda K^{-3}$$

$$D = (\beta - \varepsilon K^2)\,K^{-4} \tag{14}$$

(12) is a convenient form for computation once the α β ... have been calculated. $h_{ij}(K)$ can now be calculated from (7) and hence from (3), a_{ij}.

In terms of the constants listed in (11) we find that

$$\alpha_i = a_i + 2R_ib_i + 4dR_i^3; \qquad \alpha = a_1 + 2bR_1 + 4dR_1^2(R_{12} + 2\lambda)$$

$$\beta = 24d$$

$$\gamma_i = 2b_i + 12R_i^2 d; \qquad \gamma = 2b + 12dR_1R_2$$

$$\delta_i = R_i[R_ib_i + a_i + R_i^3 d]; \quad \delta = bR_1^2 + a_1R_{12} + R_1^3 d(R_{12} + 3\lambda)$$

$$\varepsilon_i = 2b_i; \qquad \varepsilon = 2b. \tag{15}$$

It is also possible to evaluate the long wave limit of the three partial structure factors. We find from (12) that

$$\lim_{K\to 0} c_{ii} = -4\pi R_i^3\left[a_i + \frac{b_iR_i}{4} + \frac{dR_i^3}{6}\right] \tag{16}$$

and

$$\lim_{K\to 0} c_{12} = -4\pi R_1^3\left\{\frac{b}{3}\left[R_{12} - \frac{R_1}{4}\right] + \lambda\, dR_1\left[R_{12} - \frac{R_1}{5}\right]\right.$$
$$\left. + \frac{d}{5}R_1^2\left[R_{12} - \frac{R_1}{6}\right]\right\} - 4\pi a_1R_{12}^3/3 \tag{17}$$

which agree, as they should, with $4\pi\int_0^\infty c(r)r^2\,dr$ when use is made of (8) and (9). The calculation of $h_{ij}(o)$ and $a_{ij}(o)$ is immediately accomplished by combining (16) and (17) with (7) and (3). For pure liquids, the well-known Ornstein-Zernike equation relates the long wavelength limit of the structure factor to the compressibility by

$$k_BK_TT = a(o)/\varrho = 1/\varrho + h(o) = [\varrho - \varrho^2c(o)]^{-1} \tag{18}$$

where K_T is the isothermal compressibility.

This result can be generalised for a two component liquid. It follows from the work of Kirkwood and Buff (1951) that

$$k_BK_TT = \frac{1 + \varrho_1h_{11}(o) + \varrho_2h_{22}(o) + \{h_{11}(o)\,h_{22}(o) - h_{12}(o)^2\}\,\varrho_1\varrho_2}{\varrho_1 + \varrho_2 + \varrho_1\varrho_2\{h_{11}(o) + h_{22}(o) - 2h_{12}(o)\}}$$
$$= \frac{1}{\varrho_1\{1 - \varrho_1c_{11}(o) - \varrho_2c_{12}(o)\} + \varrho_2\{1 - \varrho_2c_{22}(o) - \varrho_1c_{12}(o)\}} \tag{19}$$

5. Discussion

To test the validity of this approach we consider the equiatomic alloy, NaK, which is a relatively simple liquid alloy and for which x-ray and neutron diffraction data have been recently obtained (Henninger *et al.*, 1966). In addition data are available for the density and K_T over the whole composition range (Abowitz and Gordon, 1962). As for the one component case, the final solution will depend on the choice made of ξ, which in turn relates to the choice of R_1 and R_2. Ashcroft and Lekner found that four pure Na and pure K, a close fit with experiment was obtained with $\xi = 0.45$ so that $R_1 = 3.28$A (Na) and $R_2 = 4.06$A(K). Presumably these would alter somewhat in the alloy due to the change in electron density. However, in the absence of any theory of this effect, we shall retain these hard sphere diameters so that if the density is taken as 0.87 g cm^{-3}, which corresponds to 373°K, ξ (alloy) $= 0.451$. The evaluation of the constants is straightforward and Fig. 1 shows $a_{ij}(K)$ derived by the above expressions; the arrows indicate the positions of the first few extrema for pure Na and K calculated with the same R_1 and R_2. In Fig. 2 we compare the experimental x-ray diffraction data with the theoretical curve derived from the calculated a_{ij} and the published values of f_1 and f_2 (Hanson *et al.*, 1964). The measurement of agreement, particularly around the first peak, is encouraging and shows that for this alloy at least the P.Y. hard sphere description is a very useful first approximation.

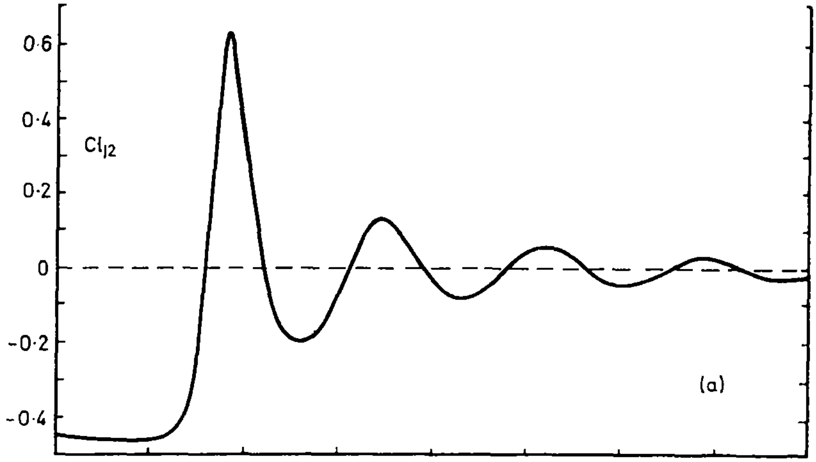

Fig. 1a

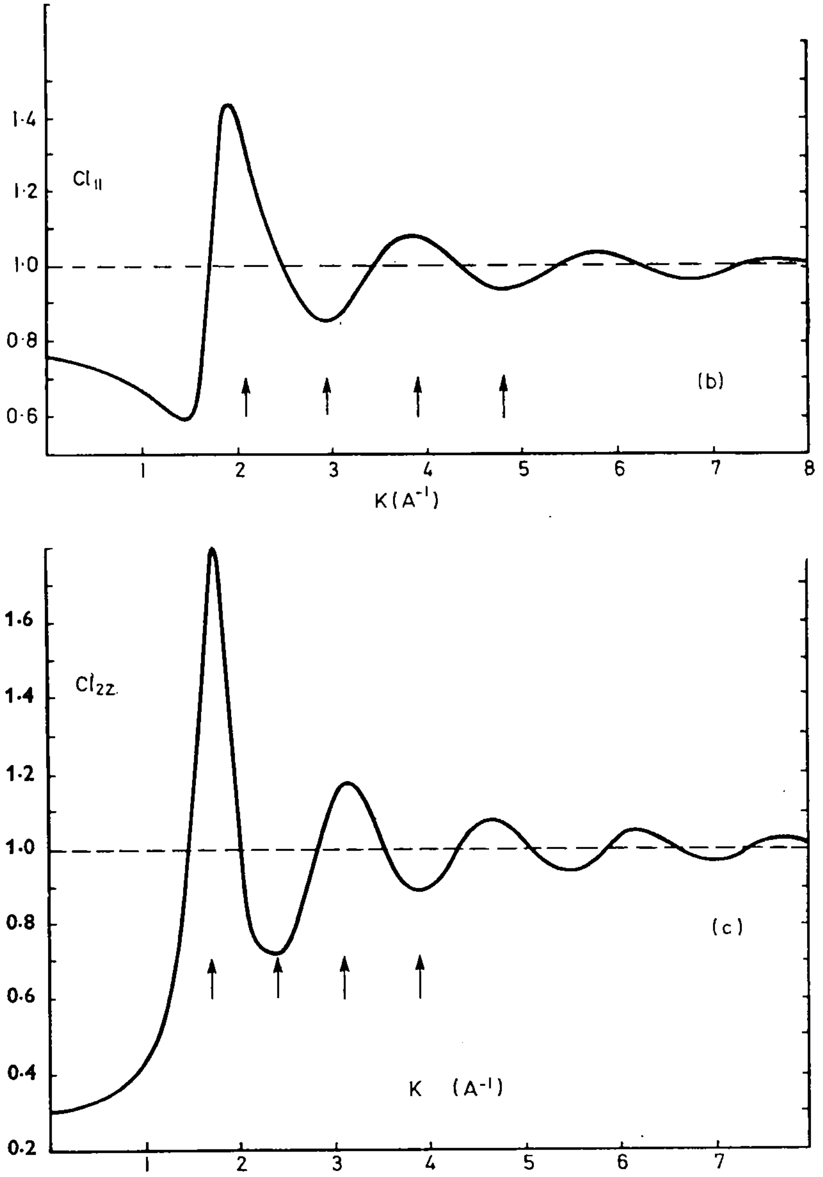

Figure 1. (a)—(c) Partial structure factors for Na–K, Na–Na and K–K respectively.
The arrows on (b) and (c) indicate the position of the first four extrema for pure Na and pure K.

Since the position of the first maximum in a_{ij} is virtually independent of m_i, we would expect the main maximum in the total x-ray curve to move monotonically from the pure Na peak to the pure K peak as m_1 varies from 1 to 0 (Eq. (2)]. This was indeed observed for Na–K alloys by Orton and Williams (1960), and corresponding behaviour for many other alloy systems has also been reported (e.g. Hg–Tl: Halder *et al*, 1966; Hg–In; Kim *et al*, 1961).

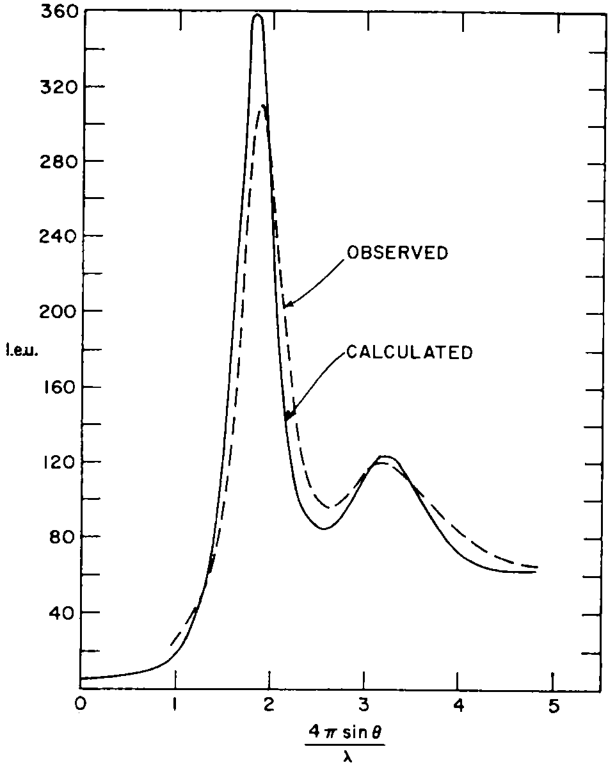

Figure 2. A comparison of the observed x-ray diffraction pattern with that calculated from the structure factors in Fig. (1).

It is worth emphasising that this model predicts that the main peak in a_{12} falls roughly midway between a_{11} and a_{22}. For certain alloys this is not the case, particularly, it seems, when the thermodynamic properties suggest a marked degree of local order. For example, the liquid alloy Cu_6Sn_5 is known to have an x-ray diffraction pattern characterised by a double-headed peak and the detailed analysis of Enderby *et al* (1966) showed that this arose because the positions of the main peaks in a_{11} and a_{12} were coincident. It might be possible to generalise the P.Y. theory to account for this in terms of the non-additivity of R_1 and R_2, but no analytic progress can yet be reported.

We finally consider the $K \to 0$ limit; although there seems to be no way of checking the individual $a_{ij}(o)$, the composite quantity which forms the right hand side of (19) can be compared experiment. The theoretical value of $k_B K_T T$ turns out to be 1.52 which compares very closely with the experimental value of 1.54 derived from the measurements of Abowitz and Gordon (1962). It is important to note that negative values of the a_{12}, when defined by (3), are not automatically excluded, although a_{ii} is positive definite. Enderby et al (1966) found that the necessary conditions which a_{ij} had to satisfy were

$$a_{ii} > 0$$

$$\text{and} \quad a_{11}a_{22} - (a_{12})^2 > 0 \quad \text{for all } K.$$

It is evident that the $a_{ij}(o)$ obtained in this work do not violate these conditions.

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