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Theory for calculation of static structures of a liquid binary alloy using neutron scattering data

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Abstract. A theory for the calculation of static structures of a liquid binary alloy, using neutron scattering data on the concentration–concentration structure factor, is proposed, together with its validity criterion. On the basis of this criterion, the result of the modified mean spherical model is critically discussed.

1. Introduction

Since Ruppersberg and Reiter (1982) suggested an approach analysing the neutron scattering data on the concentration–concentration structure factor $S_{cc}(q)$ in liquid binary alloys via the ordering potential $v(r)$, it has been investigated in many systems (see, e.g., Copestake *et al* 1983, Ruppersberg 1983, Ruppersberg and Schirmacher 1984, Hoshino and Young 1986a, 1988, Ginoza *et al* 1987). The basic assumption is also well known (Copestake *et al* 1983) (also see below). On using it, the approach has proved to be a reasonably useful tool. However, it is not always obvious whether the assumption is actually satisfied. The aim of this paper is to propose one possible theory for calculation of static structures by using the scattering data without this assumption, together with its validity criterion, and to discuss critically the result of the modified mean spherical model (MSM) (Ginoza 1987a, 1988).

Now, in the ordering potential approach mentioned above, one first calculates the following quantity $W^{\exp}(r)$ with the use of the available neutron scattering data ($S_{cc}^{\exp}(q)$) for $S_{cc}(q)$:

$$W^{\exp}(r) = \frac{1}{2\rho\beta c_1 c_2 (2\pi)^3} \int \mathrm{d}\boldsymbol{q} \left(1 - \frac{c_1 c_2}{S_{cc}^{\exp}(q)}\right) \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}) \tag{1}$$

with c_1 the type-1 ion concentration, $c_2 = 1 - c_1$, ρ the total number density and $\beta = 1/k_\mathrm{B}T$, k_B and T being the Boltzmann constant and temperature respectively. One then identifies $W^{\exp}(r)$ and $-v(r)$ for $r > \sigma$, where σ is a characteristic length such as the diameter of a hard sphere and

$$v(r) = [\varphi_{11}(r) + \varphi_{22}(r) - 2\varphi_{12}(r)]/2 \tag{2}$$

with pairwise potentials $\varphi_{ij}(r)$, modelling the interionic forces. As an example, in figure

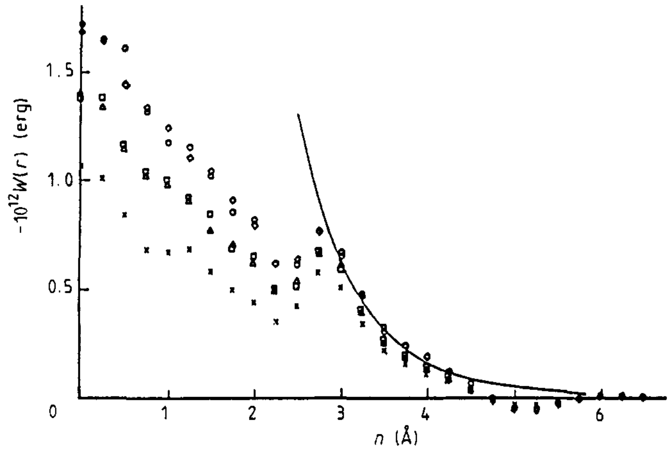

Figure 1. The function $-W(r)$ ($=-W^{\mathrm{exp}}(r)$ in the text) obtained from the neutron diffraction data of Ruppersberg and Reiter (1982) for liquid Li_4Pb at several different temperatures: ○, 995 K; ◇, 1025 K; □, 1075 K; ▲, 1125 K; ×, 1225 K; ——, fitting formula $-10^{12}W(r) = 50\exp(-1.1r)/r$ (from Copestake *et al* (1983)).

1 we show the result obtained by Copestake *et al* (1983) who investigated this approach by using the neutron scattering data of Ruppersberg and Reiter (1982) for the liquid Li_4Pb at several different temperatures, deduced the fitting formula of the long-range part of the ordering potential and obtained reasonably good static structure factors with the use of what this fitting formula suggested for $\varphi_{ij}(r)$.

2. Theory

Now, the direct correlation functions $c_{ij}(r)$ are related to the partial total-correlation function $h_{ij}(r)$ through the Ornstein–Zernike (OZ) equation

$$h_{ij}(r) = c_{ij}(r) + \rho \sum_i c_i \int \mathrm{d}\boldsymbol{r}_1\, c_{ij}(|\boldsymbol{r}_1 - \boldsymbol{r}|)h_{ij}(r_1). \tag{3}$$

With the use of this equation, $S_{cc}(q)$ can be expressed in terms of the Fourier transforms $\tilde{c}_{ij}(q)$ of $c_{ij}(r)$ as (see, e.g., Bhatia 1977)

$$c_1c_2/S_{cc}(q) = 1 - c_1c_2[\rho\tilde{c}_{11}(q) + \rho\tilde{c}_{22}(q) - 2\rho\tilde{c}_{12}(q) + f(q)] \tag{4}$$

where

$$f(q) = S_{Nc}(q)^2/\{S_{cc}(q)[S_{cc}(q)S_{NN}(q) - S_{Nc}(q)^2]\} \tag{5}$$

$S_{NN}(q)$ and $S_{Nc}(q)$ being the number–number and the number–concentration correlation functions, respectively. Corresponding to equation (1), let us define the quantity $W(r)$ as

$$W(r) = \frac{1}{2\rho\beta c_1c_2(2\pi)^3}\int \mathrm{d}\boldsymbol{q}\left(1 - \frac{c_1c_2}{S_{cc}(q)}\right)\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}). \tag{6}$$

The substitution of equation (4) into equation (6) yields

$$W(r) = [c_{11}(r) + c_{22}(r) - 2c_{12}(r) + F(r)]/2\beta \tag{7a}$$

where

$$F(r) = [(2\pi)^3\rho]^{-1} \int \mathrm{d}\boldsymbol{q}\, f(q) \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}). \tag{7b}$$

From equations (2) and (7), it is obvious that, if we assume

(i) that $f(q) \simeq 0$ for all q in equation (4) and
(ii) that $c_{ij}(r) = -\beta\varphi_{ij}(r)$ for $r > \sigma$,

we get $W(r) = -v(r)$ for $r > \sigma$ (Copestake *et al* 1983).

This is the key relation in the ordering potential approach.

As is seen from equation (5), assumption (i) will be valid provided that $S_{Nc}(q)$ is small enough in comparison with $S_{NN}(q)$ and $S_{cc}(q)$. In general, however, this assumption is not satisfied (see, e.g., Gonzalez and Silbert 1987). As for assumption (ii), this is strictly valid only as $r \to \infty$. It is, thus, not always obvious whether assumptions (i) and (ii) are satisfied. Nevertheless, it should be noted that the approach has been a reasonably useful tool. This suggests that in the vicinity of this approach there might exist a more satisfactory route by which assumptions (i) and (ii) are not always needed.

In order to incorporate the implication of $W^{\exp}(r)$ more correctly, it may be advantageous to introduce such functions $f_{ij}(r)$ that firstly they satisfy

$$W(r) = [f_{11}(r) + f_{22}(r) - 2f_{12}(r)]/2\beta \tag{8}$$

and secondly $f_{ij}(r)$ approaches $c_{ij}(r)$ as $f(q)$ approaches zero, because it is just such functions which the neutron scattering data are related to via the equation $W^{\exp}(r) = W(r)$. Corresponding to assumption (ii) in the ordering potential approach, let us define functions $\psi_{ij}^{\exp}(r)$ by

$$f_{ij}(r) = -\beta\psi_{ij}^{\exp}(r) \qquad \text{for } r > \sigma. \tag{9}$$

Note that functions $\psi_{ij}^{\exp}(r)$ are not always the interionic potentials $\varphi_{ij}(r)$. In contrast with the ordering potential approach, we can use correctly the implication of the equation $W^{\exp}(r) = W(r)$ for $\psi_{ij}^{\exp}(r)$. In particular, under the assumption of a factorisable $\psi_{ij}^{\exp}(r)$, namely

$$\psi_{ij}^{\exp}(r) = a_i a_j \psi^{\exp}(r) \qquad \text{for } r > \sigma \tag{10}$$

we get from equations (8)–(10) and $W^{\exp}(r) = W(r)$ that

$$\psi^{\exp}(r) = -2W^{\exp}(r)/(a_1 - a_2)^2.$$

It is certain that $f_{ij}(r)$ reflects any interionic correlation. Regarding the correlation, we know the exact relation

$$h_{ij}(r) = -1 \qquad \text{for } r < \sigma \tag{11}$$

but this is incomplete. Therefore, if we can find an equation relating $f_{ij}(r)$ to $h_{ij}(r)$ or $c_{ij}(r)$, equations (9) and (11) give promising closure relations for this equation, from which we can calculate the static structure factors. The equation might be obtained generally on the basis of statistical mechanics. At present, however, we do not know how to obtain it.

Now, the success of the ordering potential approach suggests that firstly the physical meaning and functional behaviour of $f_{ij}(r)$ must be very similar or close to those of $c_{ij}(r)$ and secondly the equation relating $f_{ij}(r)$ to $h_{ij}(r)$ would have the same structure as that of the OZ equation defining $c_{ij}(r)$. Noting that the OZ equation has only two system parameters (ρ and c_1 (or c_2)), we propose the following equation:

$$h_{ij}(r) = f_{ij}(r) + \rho \sum_i x_i \int \mathrm{d}\boldsymbol{r}_1 \, f_{ij}(|\boldsymbol{r}_1 - \boldsymbol{r}|) h_{ij}(r_1) \tag{12a}$$

or, with the elimination of $h_{ij}(r)$ from equations (3) and (12*a*),

$$c_{ij}(r) = f_{ij}(r) + \rho \sum_i (x_i - c_i) \int \mathrm{d}\boldsymbol{r}_1 \, f_{ij}(|\boldsymbol{r}_1 - \boldsymbol{r}|) h_{ij}(r_1) \tag{12b}$$

where x_1 and x_2 are positive-number parameters satisfying

$$x_1 + x_2 = 1. \tag{13}$$

Together with equations (9) and (11) acting as closure relations, equation (12) defines a theory for the calculation of static structures by using the neutron scattering data. It is obvious from equation (12) that, in the choice of $x_i = c_i$, $f_{ij}(r) = c_{ij}(r)$ or $f(q) = 0$, and the theory is equivalent to the work of Copestake *et al* (1983). Although we cannot give any statistical-mechanical basis for equation (12) at present, its validity and the choice of x_i may be justified by the agreement of the theory with experimental facts and the degree of self-consistency of the theory. The latter may be judged by the extent to which $W(r)$, calculated by equation (6) with the use of the theoretical structure factors, agrees with $W(r)$, given by equations (8) and (9) (a kind of sum rule!)

Now, let us consider the case of the following factorisable $f_{ij}(r)$ given by equations (9) and (10) in which, as will be shown below, we can obtain a simple criterion for the self-consistency of the theory:

$$f_{ij}(r) = -\beta a_i a_j \psi(r) \qquad \text{for } r > \sigma \tag{14}$$

where $\psi(r) = \psi^{\exp}(r)$. In this case, if we choose x_i to satisfy

$$x_1 a_1 + x_2 a_2 = 0 \tag{15}$$

we can decouple equation (12*a*) into the following two integral equations (Ginoza 1987a, 1988):

$$h_{ij}(r) = h_{\mathrm{s}}(r) - (-x_1/x_2)^{i+j-3} h_{\mathrm{a}}(r) \qquad (i,j = 1,2) \tag{16a}$$

$$f_{ij}(r) = f_{\mathrm{s}}(r) - (-x_1/x_2)^{i+j-3} f_{\mathrm{a}}(r) \qquad (i,j = 1,2) \tag{16b}$$

where

$$\begin{aligned}
&h_{\mathrm{s}}(r) = f_{\mathrm{s}}(r) + \rho \int \mathrm{d}\boldsymbol{r}_1 \, f_{\mathrm{s}}(|\boldsymbol{r}_1 - \boldsymbol{r}|) h_{\mathrm{s}}(r_1) \\
&h_{\mathrm{s}}(r) = -1 \qquad \text{for } r < \sigma \\
&f_{\mathrm{s}}(r) = 0 \qquad \text{for } r > \sigma \\
&h_{\mathrm{a}}(r) = f_{\mathrm{a}}(r) + \rho \int \mathrm{d}\boldsymbol{r}_1 \, f_{\mathrm{a}}(|\boldsymbol{r}_1 - \boldsymbol{r}|) h_{\mathrm{a}}(r_1) \\
&h_{\mathrm{a}}(r) = 0 \qquad \text{for } r < \sigma
\end{aligned} \tag{17}$$

$$f_a(r) = \beta a_1 a_2 \psi(r) \qquad \text{for } r > \sigma.$$

We can obtain from equation (16) that

$$S_{cc}(q)/c_1c_2 = 1 + (c_1c_2/x_1x_2)\{\rho\tilde{f}_a(q)/[1 - \rho\tilde{f}_a(q)]\}$$

where

$$\tilde{f}_a(q) = \int d\boldsymbol{r}\, f_a(r) \exp(i\boldsymbol{q}\cdot\boldsymbol{r}). \tag{18}$$

With the use of this expression for $S_{cc}(q)$, equation (6) becomes

$$W(r) = \frac{1}{2\rho\beta x_1 x_2 (2\pi)^3} \int d\boldsymbol{q} \frac{\rho\tilde{f}_a(q)}{1 + \Delta_0 \rho\tilde{f}_a(q)} \exp(i\boldsymbol{q}\cdot\boldsymbol{r}) \tag{19}$$

where

$$\Delta_0 = c_1c_2/x_1x_2 - 1.$$

On the other hand, equations (8) and (14) yield

$$W(r) = (a_1a_2/2x_1x_2)\psi(r) \tag{20}$$

where we used equations (13) and (15). As is discussed above, the self-consistency of the theory is judged by the extent to which equations (19) and (20) agree with each other. It is easy to show from equations (17) and (18) that, in the case of $\Delta_0 = 0$, equation (19) is equivalent to equation (20) and the self-consistency is perfect. In the application of the theory, however, we must choose the case of $\Delta_0 \neq 0$ in order to improve the theory in the light of experimental facts. As is obvious from equation (19), the self-consistency of the theory in this case may need the condition

$$|\Delta_0| \equiv \Delta \ll 1. \tag{21}$$

From equations (13) and (15),

$$\Delta = |(c_1a_1 + c_2a_2)(c_1a_2 + c_2a_1)/a_1a_2|. \tag{22}$$

Now, one of the present authors (Ginoza 1987a, 1988) proposed the modified MSM which is equivalent to the theory given by equations (12*a*) and (14). This model has been applied to binary liquid alloys (Aniya and Ginoza 1987, 1988, Ginoza 1987b, 1988). It is interesting to investigate critically these studies on the basis of the self-consistency criterion (21) obtained above.

The solution (16) yields the following relationship between $S_{NN}(q)$, $S_{Nc}(q)$ and $S_{cc}(q)$:

$$[S_{NN}(q) - S_0(q)][S_{cc}(q) - c_1c_2] = S_{Nc}^2(q) \tag{23}$$

where

$$S_0(q) = 1 + \rho \int d\boldsymbol{r}\, h_s(r) \exp(i\boldsymbol{q}\cdot\boldsymbol{r}).$$

The validity of equation (23) was discussed in the limit $q \to 0$ on the basis of available experimental results, and it was shown that the agreement of equation (23) with the experimental results is reasonably good except for at both ends of the concentration range (Ginoza 1988). Now, equation (23) is the general result corresponding to solution (16) which has no relation to the choice of concentration and potential function $\psi(r)$. However, equation (22) shows that Δ approaches unity as c_1 or c_2 approaches zero,

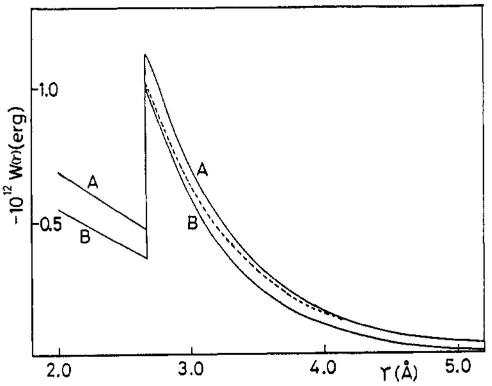

Figure 2. The function $-W(r)$ at 1075 K for $c_1 = 0.8$, $\sigma = 2.65$, $\lambda = 1.145$ and $a_1 = 0.473$: curve A, $\Delta = 0$; curve B, $\Delta = 0.02$; ---, fitting formula in figure 1.

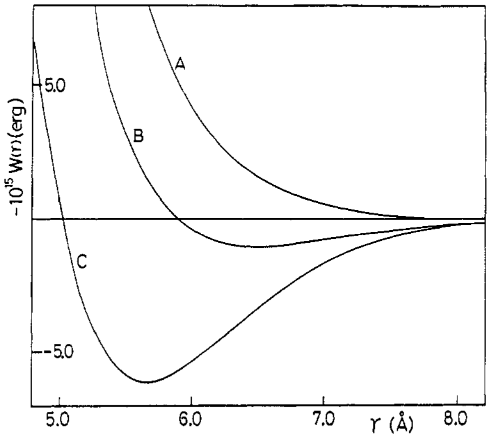

Figure 3. The function $-W(r)$ at 1075 K for $c_1 = 0.8$, $\sigma = 2.65$, $\lambda = 1.145$ and $a_1 = 0.473$: curve A, $\Delta = 0.01$; curve B, $\Delta = 0.02$; curve C, $\Delta = 0.04$.

unless $c_1a_1 + c_2a_2 = 0$ or $c_1a_2 + c_2a_1 = 0$. Therefore, equation (21) means that in both limits ($c_1 = 0$ and $c_2 = 0$) the modified MSM is, in general, inconsistent. In fact, equation (23), in the limit $q \to 0$, deviates in the neighbourhood of both ends of the concentration range from the experimental thermodynamic result (Ginoza 1988).

3. Results and discussion

Corresponding to the values of $W^{\exp}(r)$ for liquid Li_4Pb at 1075 K in figure 1, figure 2 shows the behaviour of $W(r)$ obtained from equation (6) using solution (16) with $\psi(r) = \exp(-\lambda r)/r$, where $\sigma = 2.65$, $\lambda = 1.145$, $a_1 = 0.473$ and $\Delta = 0$ for the full curve A and $\Delta = 0.02$ for the full curve B and the broken curve represents the fitting formula in figure 1. Both curve A and curve B agree reasonably well with the distribution of values of $-W^{\exp}(r)$ in figure 1. This suggests that the best agreement of the modified MSM with experiment may be attained for a parameter in the region of $0 < \Delta < 0.02$ in the case of liquid Li_4Pb. In fact, Aniya and Ginoza (1987) investigated the temperature dependence of the static structure factor of liquid Li_4Pb on the basis of the modified MSM with $\psi(r) = \exp(-\lambda r)/r$ and showed by the choice of $\Delta = 0.012$ that the obtained temperature dependence agrees reasonably well with the measured one. This value of Δ is compatible with equation (21).

In relation to figure 2, it may be worthwhile to point out the interesting behaviour of $-W(r)$ and that, for $\Delta \neq 0$, it has a negative minimum. This is shown in figure 3 with the use of a different scale for the ordinate axis. In fact, we can see in figure 1 that $-W^{\exp}(r)$ has a negative minimum for $r \simeq 5.2$ Å. Copestake *et al* (1983) suggested that such behaviour of $-W^{\exp}(r)$ should be related to the fact that liquid Li_4Pb is a metal and conduction electron screening often produces oscillatory effective pairwise interionic potentials. However, it should be recalled here that this suggestion is based on the assumption that $W^{\exp}(r) = -v(r)$.

Investigations on $S_{cc}(q)$ of the compound-forming liquid $Li_{71}Ag_{29}$ and the phase-separating liquid $Li_{61}Na_{39}$, both being zero alloys, were carried out on the basis of the modified MSM with $\psi(r) = \exp(-\lambda r)/r$ in the papers by Aniya and Ginoza (1988) and Ginoza (1987b), respectively. The self-consistency of the theories used in these papers can be analysed in the same way as above. The compatibility of the theories with equation (21) is good except in the case of producing the first minimum value of the experimental $S_{cc}(q)$ of liquids $Li_{61}Na_{39}$ by Ruppersberg and Knoll (1977). As for the origin of this failure, the works of Hoshino and Young (1986a, b, 1988) suggest that it may be related to the choice of $\psi(r)$ rather than to the framework of the modified MSM. In fact, it is impossible, even if approximately, that the choice of $\psi(r) = \exp(-\lambda r)/r$ produces $W^{\exp}(r)$ shown in figures 2(*a*) and 2(*b*) in the work of Hoshino and Young (1986a). The investigation regarding this is now in progress.

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