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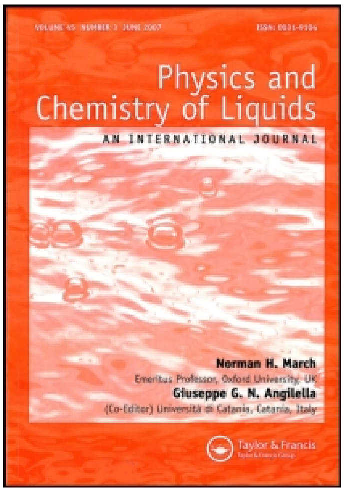

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On the Derivation of Pair Potentials From Structural Data for Metallic Glasses

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On the Derivation of Pair Potentials From Structural Data for Metallic Glasses

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The problem of extracting interatomic pair potentials from diffraction data for metallic alloy glasses is discussed and examples are given using experimentally obtained structure factors. First, three transition metal-metalloid glasses are treated approximately, as pseudo single-component assemblies with encouraging preliminary results. A second analysis, using the correct *partial* structure factors for a $Ni_{64}B_{36}$ glass, is found to be a more difficult case, which highlights the limitations of even the best current diffraction data for this purpose. The possible future extension of this work is discussed, in the context of the need for fundamental theories of metallic glass structures.

1 INTRODUCTION

One important feature of the work on simple liquid metals in the 1960's was the coordinated search for appropriate interatomic pair potentials. This problem was successfully approached from both theoretical and experimental standpoints, as the various reviews of the period make clear, see March.[1] In

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contrast, despite the considerable activity directed towards metallic glasses in the last decade, comparatively little reference has been made to interatomic pair potentials—with the possible exceptions of the pioneering work of Hafner[2] on simple metal glasses and recent work by Fujiwara[3] on transition metal—metalloid glasses. In the last few years much improved diffraction (structural) data on metallic glasses have become available at both conventional and high spatial resolution (see Ref. 4). There is a need, therefore, for reliable interatomic potentials for "relaxation" calculations and molecular dynamics simulations of these new data. It seemed to us worthwhile to investigate whether such interatomic potentials might alternatively be derived directly from structural data on metallic glasses by using the methods already established for liquid metals.

2 THE STRUCTURE FACTOR, DIRECT CORRELATION FUNCTION AND INTERATOMIC PAIR POTENTIAL

In x-ray or neutron diffraction the structure factor $S(Q)$ for a single-component system is related to the pair distribution function $g(r) = \rho(r)/\rho_0$ by

$$S(Q) = 1 + 4\pi\rho_0 \int_0^\infty r^2[g(r) - 1] \frac{\sin Qr}{Qr}\, \mathrm{d}r \tag{1}$$

where ρ_0 is the atomic number density of the system. Putting $h(r) = g(r) - 1$, this can be rewritten as,

$$S(Q) = 1 + h(Q) \tag{2}$$

Here, $h(Q)$ is the Fourier transform of $h(r)$. The Ornstein-Zernicke[5] equation for single-component fluids defines the direct correlation function, $c(r)$, through the convolution

$$h(r) = c(r) + \rho_0 \int h(r')c(|r - r'|)\, \mathrm{d}r' \tag{3}$$

which, when transformed, becomes,

$$h(Q) = c(Q) + c(Q)h(Q) \tag{4}$$

Thus, Eqs. 2 and 4 give an expression for the function $c(Q)$ in terms of the structure factor $S(Q)$

$$c(Q) = 1 - 1/S(Q) \tag{5}$$

In addition, several theories of liquid structure provide a relation between $c(r)$, $g(r)$ and the effective pair potential $\phi(r)$. The well-known Percus-Yevick[6] form is, for example,

$$\phi(r) = kT \ln\left(1 - \frac{c(r)}{g(r)}\right) \tag{6}$$

while an alternative and simpler proposal[7] is

$$\phi(r) = -kTc(r) \tag{7}$$

Hence, the transformation of $S(Q)$ to $g(r)$ and of $c(Q)$ to $c(r)$, in principle, enables $\phi(r)$ to be derived. However, as Enderby[8] and others have pointed out, the numerical instability of Eq. 5 can lead to large errors in $c(Q)$, and this is especially true for small values of Q where $S(Q)$ is normally close to zero.

3 PRELIMINARY DERIVATION OF THE INTERATOMIC POTENTIALS

A pre-requisite for the successful derivation of interatomic potentials is, as shown above, a reliable and well-defined structure factor $S(Q)$. The examples used in this preliminary analysis have been taken from the transition metal–metalloid group of glasses and these were treated as pseudo-single-component cases, using $S_{\mathrm{TMTM}}(Q)$ only, to obtain a generalised $\phi_{\mathrm{TMTM}}(r)$ potential. The structural data for the typical $\mathrm{TM}_{80}\mathrm{Met}_{20}$ glasses are, in fact, dominated by contributions from the $S_{\mathrm{TMTM}}(Q)$ partial, which can therefore usually be obtained by experiment with reasonable precision.

The $S(Q)$ curves employed were derived in our laboratory-$S_{\mathrm{FeFe}}(Q)$ curve for $\mathrm{Fe}_{83}\mathrm{B}_{17}$ glass,[9] $S_{\mathrm{NiNi}}(Q)$ from $\mathrm{Ni}_{82}\mathrm{B}_{18}$ glass,[9] $S_{\mathrm{CoCo}}(Q)$ from $\mathrm{Co}_{81.5}\mathrm{B}_{18.5}$[10] glass while an $S_{\mathrm{PdPd}}(\mathrm{Q})$ curve from $\mathrm{Pd}_{80}\mathrm{Si}_{20}$ glass, obtained from the diagrams of Fukunaga and Suzuki,[11] was used as an additional standard. These curves were first superimposed in order to gauge the possible reliability of these different data sets. The absolute peak positions in the curves were different on account of the different atomic sizes, but scaling the abscissa for the Fe–Fe and Pd–Pd curves by 1.03 and 1.12 respectively allowed the four curves to be superimposed—see Figure 1. The difference in the peak heights observed correlates very well with the variation in packing fraction η, where

$$\eta = \tfrac{4}{3}\pi\langle r^3\rangle\rho_0.$$

Here, $\langle r^3\rangle$ is calculated using the Goldschmidt radii of the metal atoms and the tetrahedral covalent radii of the metalloids, and the densities ρ_0 were obtained from published values.[12] It turns out that

$$\eta_{\mathrm{CoB}} = 0.72 > \eta_{\mathrm{NiB}} = 0.71 > \eta_{\mathrm{FeB}} = 0.69 > \eta_{\mathrm{PdSi}} = 0.68$$

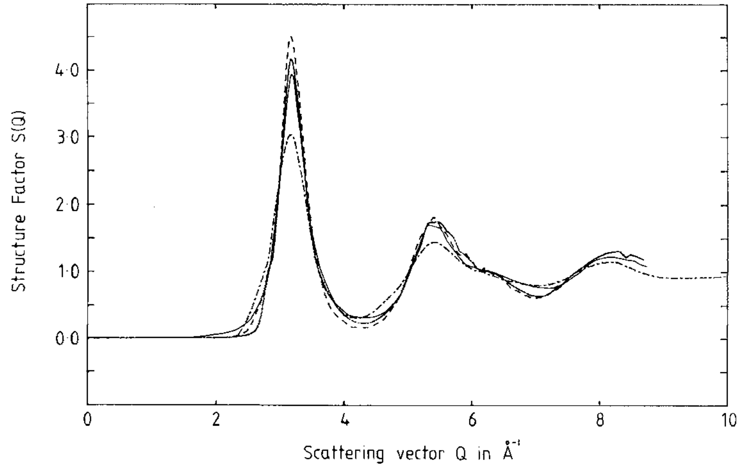

FIGURE 1 The partial structure factors $S_{TMTM}(Q)$ for the transition metal–metalloid (TM-met) glasses —·— $Pd_{80}Si_{20}$;[11] ———— $Fe_{83}B_{17}$;[9] --- $Ni_{82}B_{18}$;[9] --- $Co_{81.5}B_{18.5}$.[10] The ordinates for the $S_{FeFe}(Q)$ and $S_{PdPd}(Q)$ curves have been scaled to expedite their intercomparison, as described in the text.

and Figure 1 shows a similar trend in the heights of the peaks in $S(Q)$. Since these $S(Q)$ curves appeared to be so mutually consistent, they were used individually to obtain potential curves, as explained below, rather than as an averaged $S_{TMTM}(Q)$ curve, as originally planned. The $c(Q)$ curves were defined, through Eq. 5, from the $S(Q)$ curves given in Figure 1. The experimental $S(Q)$ values were generally unreliable below about $Q \approx 0.5$ A^{-1} so that the data had to be extrapolated down to $S(O)$ as a slowly decreasing function. The absence of data in this region is not so serious for liquid samples, providing the long-wavelength limit $S(O)$ can be evaluated from ρ_0 the number density and χ_T the isothermal compressibility[1]

$$S(O) = \rho_0 k_B T \chi_T \tag{8}$$

However, the extent to which this result is valid for glasses is not well established.[13] Furthermore, experimentally measured compressibilities are not so readily available for these glasses as they are for certain liquid metals. Working on the hypothesis that for glasses the compressibility limit, Eq. 8, might be in error by a factor of about two,[13] while the use of compressibility data extrapolated from the parent materials might provide an additional similar uncertainty, substitution (8) then leads to values of $S(O) \approx 0.002$ for the three $S(Q)$ curves examined. The experimental curves for higher Q values were therefore smoothly extrapolated to this value. The Fourier transform of $c(Q)$ leads, through the simplified result of Eq. 7, to the potential curves shown in Figure 2, which will be discussed below.

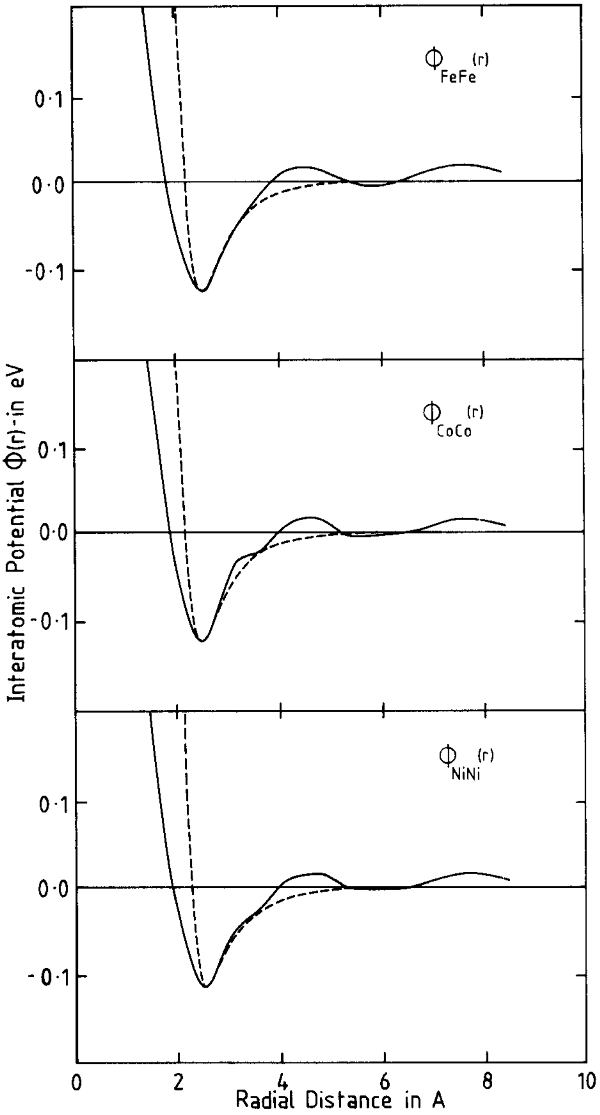

FIGURE 2 Interatomic pair potentials derived from the structure factors shown in Figure 1. The dashed curves are 6–12 potentials, fitted to the minima of the experimental potential wells.

4 BINARY METALLIC GLASSES

The mathematical relations given in Section 3 can be readily generalised to cover a multicomponent fluid—specifically here the binary case. The total structure factor can be written:

$$S(Q) = 1 + 4\pi\rho_0 \sum_i^2 \sum_j^2 \frac{x_i x_j \beta_i \beta_j}{\langle\beta\rangle^2} \int_0^\infty r^2 h_{ij}(r) \frac{\sin Qr}{Qr}\, \mathrm{d}r \tag{9}$$

Here, the symbol β represents the scattering amplitude, either the nuclear scattering length b in neutron diffraction, or the atomic scattering factor $f(Q)$ in X-ray diffraction. The atomic concentrations are x_i and $x_j = 1 - x_i$ and $\langle\beta\rangle$ is the average $(x_i\beta_i + x_j\beta_j)$. The partial structure factors[14] are defined through the equation

$$S_{ij}(Q) = 1 + 4\pi\rho_0 \int_0^\infty r^2 h_{ij}(r) \frac{\sin Qr}{Qr}\, \mathrm{d}r = 1 + h_{ij}(Q) \tag{10}$$

so that

$$S(Q) = \sum_i \sum_j w_{ij} S_{ij}(Q) \tag{11}$$

where the weighting factors w_{ij} are as shown within the double summation of Eq. 9.

The partial direct correlation functions $c_{ij}(r)$ may be written,[15]

$$h_{ij}(r) = c_{ij}(r) + \sum_{l=1,2} \rho_l \int h_{il}(r') c_{lj}(|r - r'|)\, dr' \tag{12}$$

where Eq. 12 is in fact in the form used by Lebowitz[16] and $h_{ij} = h_{ji}$ and $c_{ij} = c_{ji}$. When these four equations are transformed, this gives four equations of the type.

$$h_{11}(Q) = c_{11}(Q) + x_1 h_{11}(Q) c_{11}(Q) + x_2 h_{12}(Q) c_{21}(Q) \tag{13}$$

These then simply lead to expressions for the $c_{ij}(Q)$ in terms of the partial structure factors $S_{ij}(Q)$, omitting the Q dependence for brevity,

$$\begin{aligned} c_{11} &= [(S_{11} - 1)(1 + x_2(S_{22} - 1)) - x_2(S_{12} - 1)^2]/D \\ c_{12} &= (S_{12} - 1)/D \\ c_{22} &= [(S_{22} - 1)(1 + x_1(S_{11} - 1)) - x_1(S_{12} - 1)^2]/D \end{aligned} \tag{14}$$

The denominator in the above equations is given by

$$D = [1 + x_1(S_{11} - 1)][1 + x_2(S_{22} - 1)] - x_1 x_2 (S_{12} - 1)^2 \tag{15}$$

This factor D can have values close to zero and its general form is similar to that of a partial structure factor.

Again, in direct comparison with the one-component case the interatomic pair potentials may be obtained from the Fourier transforms of the $c_{ij}(Q)$. Lebowitz[16] for example, has shown that the generalised form of Eq. 6 is simply

$$\phi_{ij}(r) = kT\ln\left(1 - \frac{c_{ij}(r)}{g_{ij}(r)}\right) \tag{16}$$

while,

$$\phi_{ij}(r) = -kTc_{ij}(r) \tag{17}$$

has also been suggested,[17] in analogy with Eq. 7.

An attempt was made to derive these $\phi_{ij}(r)$ starting from the three partial structure factors $S_{\mathrm{NiNi}}(Q)$, $S_{\mathrm{NiB}}(Q)$, $S_{\mathrm{BB}}(Q)$ for the high boron glass $\mathrm{Ni_{64}B_{36}}$. These were obtained by us from a neutron diffraction experiment on isotopically enriched samples, as described elsewhere.[18] Although this is a favourable case for the derivation of the $S_{ij}(Q)$, it proved to be very difficult to obtain reliable potentials. Each $c_{ij}(Q)$ curve depends on differences between the $S_{ij}(Q)$, Eqs. 14, and if errors in the $S_{ij}(Q)$ allow changes of sign to occur in the term D, harmful singularities occur in the $c_{ij}(Q)$. This emerges to be more important than any uncertainty over the long-wavelength limits of the $S_{ij}(Q)$.

However, the term D is the same function as that which occurs in the derivation of the so-called "uncertainty relations" for the practical limits of the $S_{ij}(Q)$. These limits arise because the total scattered *intensity* can never have a negative value. Now, in the early determinations of partial structure factors it was frequently necessary to use the uncertainty relations as constraints on the experimental data although, with improvements in statistical reliability, this is not true of most present-day experiments. However, because the derivation of the potential functions is one further stage in the data analysis, it was found necessary here to introduce similar constraints to the term D, in order that it remained positive. Figure 3 shows the experimentally derived $\phi_{\mathrm{NiNi}}(r)$ curve for $\mathrm{Ni_{64}B_{36}}$ glass obtained using Eq. 17. This is actually one of the best, rather than a representative, example of the potential curves that it has been possible to obtain to date and will be discussed in detail below.

5 INTERATOMIC PAIR POTENTIALS

The approximate potential curves shown in Figure 2, can be thought of as general $\phi_{\mathrm{TMTM}}(r)$ potentials which probably determine the overall topology of the glass structures involved. The most satisfying features of these curves are the well-developed minima which occur at $r_0 = 2.58$ Å for $\phi_{\mathrm{FeFe}}(r)$ and

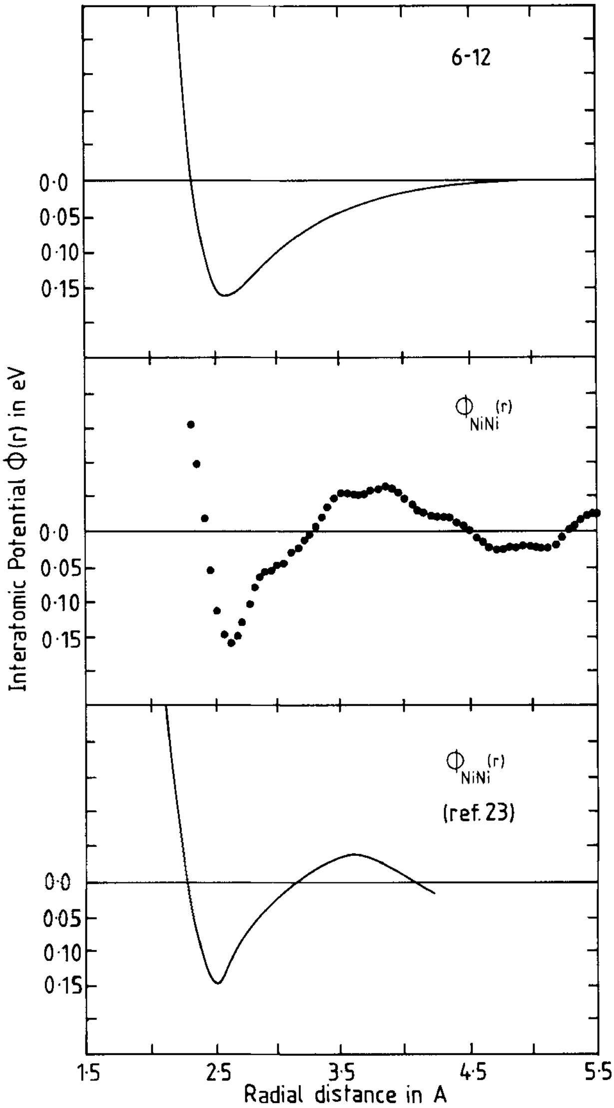

FIGURE 3 The interatomic pair potential $\phi_{NiNi}(r)$ derived from the partial structure factor $S_{NiNi}(Q)$ (Ref. 18) is shown together with a 6-12 potential, and that obtained for liquid nickel by Mitra.[23]

$r_0 = 2.56$ Å for both $\phi_{NiNi}(r)$ and $\phi_{CoCo}(r)$. These values are about 2–3% greater than the Goldschmidt diameters of the atoms involved. The scaling of the abscissa in Figure 3 is influenced by the choice of temperature, through Eq. 7. Assuming, with Hafner,[2] that the glass is truly an undercooled liquid there are at least two possible choices of characteristic temperature. First, is the effective quenching point, which may be taken approximately as the glass transition temperature T_g; this lies typically in the range $\sim$0.5–0.65 T_m for metallic glasses.[19] However, an important post-quenching stage may occur when the hot ribbon leaves the quenching roller and still undergoes annealing and structural relaxation in air, at temperatures below T_g. Alternatively, room temperature can be taken as the possible end-point of the undercooling, and Hafner[2] has used a characteristic temperature of 25°C in this way. In fact, when this latter choice is substituted into Eq. 7, it leads to realistic well-depths $\varepsilon \approx 0.136$ eV ≈ 10 mRy for each of the three curves. This compares favourably with the well depth of $\phi_{MgMg}(r) \approx 5$ mRy obtained[2] for a $Mg_{70}Zn_{30}$ glass. These well depths also scale reasonably with the liquidus temperatures of the TM-met and $Mg_{70}Zn_{30}$ glasses.

The form of the $\phi(r)$ curves in Figure 2 is illustrated by means of superimposed 6–12 potentials. The agreement is reasonable for $r \gtrsim r_0$ but clearly the repulsive core is poorly reproduced. One possible reason for this is that the relations between $\phi(r)$ and $c(r)$, Eqs. 6, 7 and 16, 17 are actually asymptotic results and not expected to be valid at small r values.[1] A second possibility arose from the trial extrapolations of $S(Q)$ to $S(O)$, which showed that the region of $S(Q)$ near the onset (foot) of the first maximum influenced the steepness of the $\phi(r)$ curve. Now, we have already established that this same region of $S(Q)$ is particularly influenced by the post-quench annealing, referred to above (see Ref. 20, Figure 2). Thus, if this post-quench annealing relaxes the glass structure away from that of a true supercooled liquid, then the relations between $S(Q)$ and $\phi(r)$ discussed above may be inapplicable and the resulting $\phi(r)$ less meaningful.

Finally, all three $\phi(r)$ curves in Figure 2 show distinct oscillations at large r, which appear to be real. They are however not compatible with the familiar Friedel oscillations which would follow a $\cos(2k_F r)/r^3$ dependence since this and the identity $Q_1 = 2k_F$ for the position of the first peak in $S(Q)$,[2,21] would lead to two different k_F values. However, the position of the first (and second) maximum with respect to the potential minimum $r_1/r_0 \approx 1.78$ (and $r_2/r_0 \approx 2.95$) agrees well with those values obtained elsewhere from the potentials for liquid gallium,[22] $r_1/r_0 \approx 1.72$ and for liquid copper[23] $r_1/r_0 \approx 1.73$.

The curve $\phi_{NiNi}(r)$ derived from the $Ni_{64}B_{36}$ data also shows a reasonable well at $r_0 = 2.58$ A, having depth $\varepsilon \approx 0.16$ eV providing, again, that a characteristic temperature 300 K is used in Eq. 7. The experimental curve is shown in Figure 3 together with a 6–12 potential and that for liquid nickel obtained from diffraction data and calculation by Mitra[23] and for which $\varepsilon = 0.129$ eV. This curve and the experimental one both show oscillations at large r but, as above, the origin of these oscillations cannot be uniquely identified. There is also a shoulder on the side of the experimental potential well at $r \approx 2.8$ A. Both this shoulder and the positive oscillation in $\phi(r)$ are similar to features observed in the curve $\phi_{\mathrm{Ga}}(r)$ obtained recently by Schommers,[22] again from experimental data—although the radial scale in this latter curve is different from the present $\phi_{\mathrm{NiNi}}(r)$ case.

6 CONCLUSION

New information on interatomic potentials for metallic glasses is necessary (a) for relaxation calculations on conventional models, whether built using dense random packings of hard spheres or local structural units, (b) for molecular dynamics simulations and (c) for the possible extension of structural calculations on *simple* metal glasses[2] to other examples. The present analysis was initiated with this need in mind. The results are admittedly preliminary but clearly some of the features of the $\phi(r)$ curves obtained can be incorporated into potentials for future calculation, in the same way that "composite" potentials have often been used for liquid metals in the past. It is unfortunate that the experimental data do not yet allow an unequivocal determination of the three interatomic pair potentials of a binary glass to be made. If these were available it would allow those constraints, which are sometimes introduced into models in an arbitrary way, to be investigated at a more fundamental level. It is hoped that the present preliminary results will draw attention to this possibility and stimulate other approaches in this area.

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