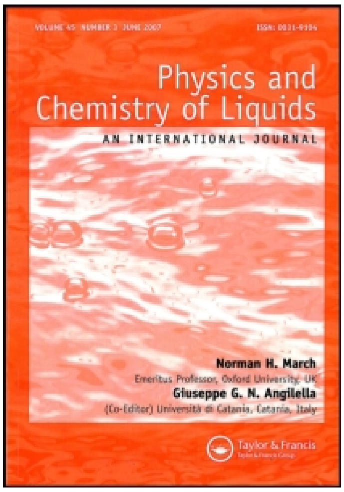

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Properties of glass-forming metallic liquids: when is there a hard-sphere-like behaviour?

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REVIEW ARTICLE

Properties of glass-forming metallic liquids: when is there a hard-sphere-like behaviour?

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Chathoth and coworkers (Phys. Rev. Lett. **101**, 037801 (2008)) have reported examples of multicomponent glass-forming metallic liquids in which the packing fraction appears to be a dominant parameter. Here, we first summarise, for 15 pure liquid metals, properties of the Ornstein–Zernike direct correlation function $c(r)$ which provide a necessary, though not sufficient, condition for hard-sphere-like (HS) liquid behaviour. Returning to multicomponent melts, NiNb and NiNbSn systems have been studied by Chathoth and coworkers. Pure Ni, according to $c(r)$ data near melting, satisfies the necessary condition for HS behaviour, while Sn certainly does not. But the Sn concentration is low in the metallic glass-forming liquid NiNbSn investigated by Chathoth and coworkers. Suitable experimental diffraction data to obtain $c(r)$ in pure liquid Nb seems not to be available presently. Finally, a brief discussion is given of atomic transport in supercooled multicomponent metallic liquids, the status of the Stokes–Einstein relation being one focus.

Keywords: metallic glasses; liquid alloys; packing fraction; hard spheres; shear viscosity; atomic transport

I. Introduction

The present study of multicomponent glass-forming metallic liquids has been motivated by the very recent work of Chathoth *et al.* [1]. $Ni_{59.5}Nb_{40.5}$ and $Ni_{60}Nb_{34.8}Sn_{5.2}$ melts in particular were focused on in their investigation of atomic dynamics and a lot of attention was given to the packing fraction as the dominant parameter. In fact, these two alloys exhibit extraordinarily high packing fractions, higher than in any other alloy melts. Atomic hard-sphere (HS) diameters are usually employed in the definition of the packing fraction. This has led us to consider the importance in multicomponent glass-forming metallic liquids of HS-like behaviour in relation to long-range attractive components of the interatomic forces involved.

A natural starting point then seemed to be to examining force-field properties of pure liquid metals. Therefore, we first took the earlier data [2] in which compressibility measurements were combined with experimental diffraction data on the liquid structure

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factor [3] $S(q)$ for 15 liquid metals, the results being collected in Section 2. With the exception of Ga, Sn and Pb, the metals studied satisfy in a fair way the usual criteria for HS behaviour. Sections 3 and 4 then consider the pure metals, and in particular liquid Ni, in relation to the multicomponent metallic systems investigated by Chathoth *et al.* [1]. Appeal is also given to the theoretical study of Hausleitner and Hafner [4], where interatomic forces were derived for a particular NiNb metallic liquid. Then in Section 5 a brief discussion of dynamics is given, some attention being first focused on the relation [5] between shear viscosity η and configurational entropy S_E. The latter quantity, in turn, is related to the static structure of the glass-forming metallic liquids under consideration. Some discussion is also given to the status of the Stokes–Einstein relation (SER) [3] in liquid metallic alloys. Section 6 constitutes the summary, together with some proposals for future directions which should prove fruitful.

2. Nature of interatomic forces and the supercooling of monatomic liquid metals

An important step forward in the theoretical understanding of some properties of dense monatomic liquids like insulating Ar or metallic Na was taken when one of the prominent approximate theories of liquid structure, going back to Percus and Yevick (PY) [6], was solved analytically [7,8]. Bernasconi and March [2] focused attention on the experimentally accessible Ornstein–Zernike direct correlation function $c(r)$ [3]. This, in turn, is connected via its Fourier transform (FT) $c(q)$ with the liquid structure factor $S(q)$ by:

$$c(q) = \frac{S(q) - 1}{S(q)}. \tag{1}$$

$S(q)$ is, in essence, the FT of the pair correlation function $g(r)$ of the monatomic liquid under consideration, and can be obtained by diffraction experiments, especially using X-rays.

In early work, Johnson and March [9] and Johnson *et al.* [10] pointed out that an intimate asymptotic connection exists between $c(r)$ at large r and an (assumed) central pair potential, $\phi(r)$, namely

$$c(r) \to -\frac{\phi(r)}{k_B T}, \tag{2}$$

for $r \to \infty$, where $k_B T$ denotes the thermal energy. Returning now to the PY solution for HS, Bhatia and March [11] demonstrated that for the HS model, the direct correlation function, denoted by $c^{PY}_{HS}(r)$, had the rather remarkable property that

$$c^{PY}_{HS}(q = 0) = 1 + c^{PY}_{HS}(r = 0). \tag{3}$$

Furthermore, from [7,8] it was already known that

$$c^{PY}_{HS}(r = 0) = -\frac{(1 + 2p_f)^2}{(1 - p_f)^2}, \tag{4}$$

where p_f is used to denote the packing fraction defined by

$$p_f = (\pi/6)n\sigma^3, \tag{5}$$

σ being the HS diameter and n the atomic number density. For many simple liquids near freezing it is well known that p_f is approximately equal to 0.45, and inserting this into Equation (4) yields:

$$c_{\mathrm{HS}}^{\mathrm{PY}}(r=0) \approx -40. \tag{6}$$

Hence, from Equations (3) and (6), Bernasconi and March [2] stressed that a necessary, though not sufficient, condition for HS behaviour was that the ratio R given by:

$$R = \frac{c(r=0)}{c(q=0)}, \tag{7}$$

be approximately unity. In [2], $c(r=0)$ was calculated from experimental diffraction data for $S(q)$, using Equation (1), for 15 liquid metals near freezing. The quantity $c(q=0)$ in the denominator of Equation (7) is more readily accessible, since it is given, via Equation (1), by fluctuation theory using

$$S(q=0) = nk_{\mathrm{B}}TK_T, \tag{8}$$

where K_T is the isothermal compressibility. The findings of [2] are then collected in Table 1.

Of the 15 liquid metals in Table 1, the ratio R is far from unity in only three cases: the polyvalent metals Ga, Sn and Pb. These are therefore unambiguously of non-HS-like character. Six liquid metals, Na, K, Rb, Ag, Au and Fe have R values between 0.9 and 1.1, and therefore satisfy well the necessary criterion for HS-like behaviour. More recently, in a review by Krishnan and Price [12], their Figure 23, made possible from data obtained by levitation and X-ray experiments, shows that a further four liquid metals satisfy a (different) necessary condition for HS-like behaviour. These include three of the metals already entered in Table 1 of the present article, namely Cu, Al and Ni, plus a fourth one, Zr. In summary, from [2] and [12] we conclude that, with the clear exceptions of non-HS-like behaviour in Ga, Sn and Pb, only two metals in Table 1, namely Cs and Co, are in doubt as to the satisfaction of the necessary criterion $R \approx 1$ for HS-like behaviour.

Table 1. Direct correlation function data for pure liquid metals near freezing.

Metal	$-c(r=0)$	$-c(q=0)$	$\frac{c(r=0)}{c(q=0)}$
Na	43	41	1.0
K	42	40	1.0
Rb	45	42	1.1
Cs	50	38	1.3
Cu	60	47	1.3
Ag	51	53	1.0
Au	35	38	0.9
Mg	31	39	0.8
Al	45	54	0.8
Ga	34	200	0.2
Pb	44	110	0.4
Sn	40	140	0.3
Fe	46	48	1.0
Ni	41	50	0.8
Co	35	50	0.7

3. Binary liquid metallic alloys

Having discussed the possible classification of liquid metals into HS-like and non-HS in the previous section, let us turn to the glass-forming binary metallic alloys considered by Chathoth *et al.* [1]. Our first focus then is on NiNb. While in Section 2, Ni is concluded to be a possible HS-like metal, we do not know of the existence of diffraction measurements on pure liquid metal Nb to date. Therefore we turn to theoretical studies at this point, prominent among which is the work of Hausleitner and Hafner [4]. These authors note that there are only two crystalline phases in the Ni–Nb alloy: a tetrahedrally close-packed phase (Fe_7W_8-type) in the range 42–48 atomic per cent Ni, and the Ni_3Nb phase which crystallises in the Cu_3Ti structure, based on the stacking of close-packed layers. In the tetrahedrally close-packed phase, the larger Nb atoms are 12-, 14-, 15- and 16-fold coordinated in the form of icosahedra and Frank–Kasper polyhedra [13], the smaller Ni atoms having an icosahedral surrounding. It is noteworthy that the nearly-free-electron tight-binding-bond (NFE–TBB) approach to the interatomic forces used in [4] to model metallic glasses shows, within the series of Ni–Y, Ni–Zr and Ni–Nb amorphous alloys, a gradual change from a trigonal prismatic to a polytetrahedral topological short-range order and a decreasing chemical short-range order. Also, increasing Ni content gives rise to a transition from prismatic to tetrahedral coordination. The trend in the results for Ni–Y, Ni–Zr and Ni–Nb supports then the importance of the packing fraction, as stressed by Chathoth *et al.* [1] with reference to the Ni–Nb metallic glass.

Via Equation (2), we stress that the tail (i.e. the large r behaviour) of the direct correlation function $c(r)$ of a pure liquid metal provides important information on the long-range form of the (assumed) pair potential $\phi(r)$. We note next that Cowlam *et al.* [14,15] have generalised this approach using diffraction data on disordered binary alloys. By generalising Equation (2) to a binary liquid alloy, one has

$$\phi_{ij}(r) = -k_B T c_{ij}(r), \tag{9}$$

for $r \to \infty$, where $\phi_{ij}(r)$ represents the three interionic pair potentials in the two-component alloy, with $c_{ij}(r)$ the partial direct correlation functions. These partial c_{ij}s, written now in q-space as $c_{ij}(q)$, are related to the partial structure factors $S_{ij}(q)$ by [16]:

$$\begin{aligned} c_{11}(q) &= \frac{(S_{11}(q)-1)(1+x_2(S_{22}(q)-1)) - x_2(S_{22}(q)-1)^2}{D}, \\ c_{12}(q) &= \frac{S_{12}(q)-1}{D}, \\ c_{22}(q) &= \frac{(S_{22}(q)-1)(1+x_1(S_{11}(q)-1)) - x_1(S_{12}(q)-1)^2}{D}. \end{aligned} \tag{10}$$

The denominator D is given by:

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

Cowlam *et al.* [15] have estimated $\phi_{NiNi}(r)$ for the binary glass $Ni_{64}B_{36}$ from neutron diffraction measurements [14] of $S_{NiNi}(q)$, $S_{NiB}(q)$ and $S_{BB}(q)$ on isotopically enriched samples, and their interatomic potential is re-drawn in Figure 1. There is a characteristic metallic-like repulsive hump after the principal minimum, followed by a further, rather shallow attractive region. This approach offers clear possibilities for future diffraction studies in binary metallic glasses, even though Cowlam *et al.* [15] stress the preliminary

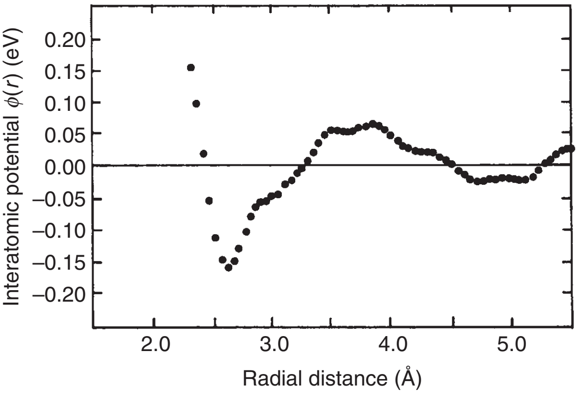

Figure 1. Interatomic pair potential $\phi_{\mathrm{NiNi}}(r)$ derived by Cowlam *et al.* from the measured partial structure factors $S_{ij}(q)$ in a $Ni_{64}B_{36}$ glass. Re-drawn from [15].

nature of their $\phi_{\mathrm{NiNi}}(r)$. It is of obvious interest for the future to test whether the first attractive region especially of Figure 1 appreciably alters any properties of the HS approximation to the $Ni_{64}B_{36}$ metallic glass.

To complete this section we mention briefly some other systems on which useful data are available. Thus, for the transition metal–metalloid glass $Pd_{80}Si_{20}$, experimental partial structure factors are available from the work of Fukunaga and Suzuki [17] (see also [18]). Returning to the packing fractions p_f, but now in liquid binary alloys, diffraction peak heights in CoB, NiB, FeB and PdSi glasses correlate well with p_f, in the order $p_f(\mathrm{CoB}) = 0.72 > p_f(\mathrm{NiB}) = 0.71 > p_f(\mathrm{FeB}) = 0.69 > p_f(\mathrm{PdSi}) = 0.68$, where the packing fraction is now taken to be defined by:

$$p_f(\mathrm{alloy}) = (4/3)\pi\langle r^3\rangle n. \tag{12}$$

In this equation, the averaged value $\langle r^3\rangle$ is calculated using the Goldschmidt radii of the metal atoms and the tetrahedral covalent radii of the metalloids, and the number densities n are obtained from Lamparter *et al.* [19]. Though the above values of the packing fractions may well be correct in the form of inequalities, the above p_f values are much higher than the values for the alloys in the work by Chathoth and coworkers, and we expect reductions in future work. We turn immediately below to display results for a few selected examples of multicomponent glass-forming metallic liquids.

4. Multicomponent glass-forming metallic liquids

Since multicomponent systems in the present context now represent a huge area of both basic and technological interest, we must inevitably be very selective in this section. Returning to the basic motivation provided by the recent work of Chathoth *et al.* [1], let us begin with the NiNbSn melts. While the discussion in Section 3 indicates that the binary liquid alloy NiNb may subsequently prove to qualify as a possible HS-like material, Sn is one of the pure liquid metals discussed in Section 2 that is certainly non-HS-like. Of course, at low concentrations of Sn the situation may not be appreciably changed, but as the Sn concentration is increased we can expect important interplay between packing fraction effects from largely repulsive interactions and long-range tails having characteristic metallic forms following the principal minimum in the pair potential. It may be that future studies can clarify whether (1) repulsive interactions and long-range tails both contribute to empirical packing fractions, or (2) packing fraction effects come from repulsive, or at least short-range, interactions and long-range tails disturb those effects. The alternative seems to be that (3) the two effects are independent.

As a second example of multicomponent melt we take the glass forming ZrTiNiCuBe alloys, which have been investigated by incoherent, quasi-elastic neutron scattering [20]. In particular, neutron data was obtained on $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ and on $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ melts. These alloys not only exhibit a remarkable stability against crystallisation in the supercooled liquid state [21], but have viscosities (see also Section 5) at the liquidus temperature that are three or four orders of magnitude greater than in simple metallic liquids. As already summarised in Section 2, pure liquid metals Zr, Cu and Ni satisfy the necessary condition for HS-like behaviour. Presently we have no information on Ti in this respect, but there is theoretical work on the interatomic forces in metallic Be by Perrot and March [22]. This study used electron theory to construct a pair potential $\phi(r)$ in liquid Be near freezing, which is shown in Figure 2. As is quite clear in this figure, there are important metallic-like tails following a rather hard core repulsive region. Though the Be concentration only ranges from about 20 to 30% in the two alloys investigated using neutrons [20], we may well be dealing here with two alloys which have less dominant contributions from the packing fraction.

A further multicomponent glass-forming alloy of interest is $Pd_{43}Ni_{10}Cu_{27}P_{20}$, with now a non-metallic component, P. However, we defer further discussion of this material to the following section on transport. In a more general context we refer to the survey by Greer [23] on metallic glasses, where the metallic glass $W_{60}Ir_{20}B_{20}$ is cited [24]. Liquid B is now known from the levitation and diffraction studies of Krishnan and Price [12] to be metallic, and we can safely anticipate that it will show non-HS-like behaviour because of its chemical bonding propensities (e.g. compare with liquid metal Si). With this somehow arbitrary selection of multicomponent glass-forming metallic liquids, we turn from the discussion of static structure and forces to deal with transport properties.

5. Mass and momentum transport in glass-forming metallic liquids

5.1. *Diffusion via cooperative motion of numerous atoms*

Let us begin the discussion of transport in glass-forming alloys by briefly setting out phenomenology on diffusion for a multi-component liquid alloy. This can be traced back, at very least, to the book by Glasstone *et al.* [25]. Combining this background with (a) the idea of cooperative motions of numerous atoms involved in the theory of the glass transition going back to Adam and Gibbs [5] and (b) the treatment of the isotope effect by Vineyard [26], one is led by phenomenology to the form of an expression for the isotope effect on diffusion going back to Mullen [27], namely:

$$E = (D_\alpha / D_\beta - 1)\left[(m_\alpha / m_\beta)^{1/2} - 1\right]. \tag{13}$$

In this equation, m_α and m_β denote the atomic masses of the tracers, and D_α, D_β are the corresponding diffusivities. Such an approach has been employed by Faupel *et al.* [28] to analyse their experimental data of Co diffusion in the multicomponent metallic glass $Co_{76.7}Fe_2Nb_{14.3}B_7$. In this case the tracers are Co-57 and Co-60, and within their

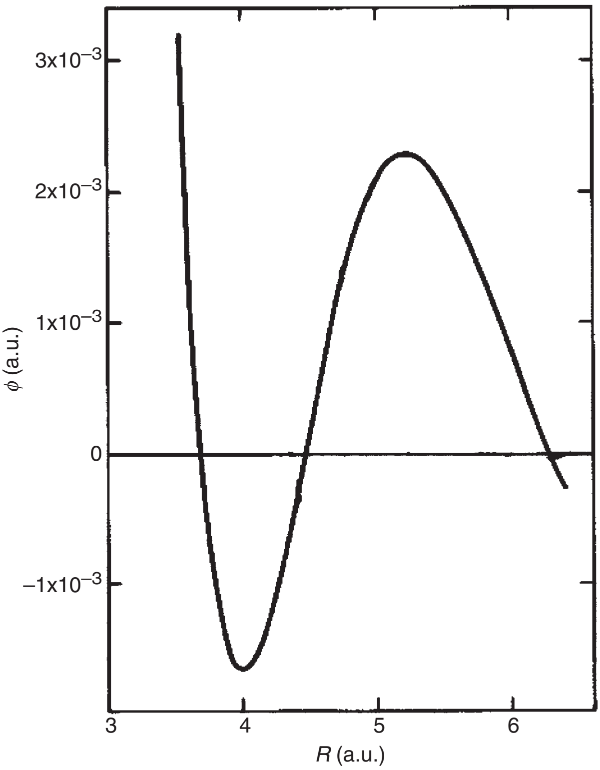

Figure 2. Calculated interatomic pair potential for liquid Be near freezing. Re-drawn from [22].

experimental accuracy, no pressure dependence of Co diffusion was found in this metallic glass. The measured value of the isotope effect E was equal to 0.1. The factor $(D_\alpha/D_\beta - 1)$ appearing in Equation (13) can then be written in the form [27]:

$$\frac{D_\alpha}{D_\beta} - 1 = \left[\left[\frac{m_\beta + (n-1)m}{m_\alpha + (n-1)m} \right]^{1/2} - 1 \right] f \Delta K, \tag{14}$$

where m is the average atomic mass of the matrix. In the picture of cooperative motions of numerous atoms involved in glassy behaviour, n denotes the number of jumping atoms, f is a correlation factor introduced initially by Bardeen and Herring [29] while ΔK accounts for many-body effects [26]. Explicitly (see also [30]), ΔK is the fraction of kinetic energy associated with motion parallel to the jump direction in the saddle-point configuration which resides in the n jumping atoms. For self-diffusion via monovacancies, $n = 1$, and then the correlation factor f solely depends on the lattice geometry, being 0.782 for the face-centred cubic (fcc) structure [31]. Faupel and coworkers obtained from their data on fcc Co that $E = 0.74$. In sharp contrast, for amorphous $Co_{76.7}Fe_2Nb_{14.3}B_7$ they obtained, as indicated above, $E = 0.10 \pm 0.01$. These authors point out that whether the weak isotope effect is basically due to a large n in Equation (14) or to a small value of ΔK cannot be concluded decisively from their measurements. However, they note that one obtains a lower limit $n \approx 10$ for the participating number of atoms in the diffusion process by assigning the entire effect to n.

Faupel and coworkers also stress that the absence of pressure dependence for Co diffusivity in $Co_{76.7}Fe_2Nb_{14.3}B_7$ shows that diffusion is not via thermal quasi-vacancies. They also note, due to similar effects which hold for diffusion of all elements except H in the metallic glasses studied [32], that it is tempting to propose such cooperative motion of atoms in amorphous alloys in general. However, the number of atoms involved must then be anticipated to vary from one material to another. This prompts us to refer to theories of cooperative motion begun by authors such as Zwanzig [33] and Nossal [34], but, though fundamentally based, much future effort will be required from first-principles to bring these theories into contact with explicit experimental results such as those of Faupel and coworkers. With this major example on mass transport in a metallic glass, we extend this section by turning next to results for shear viscosity.

5.2. *Shear viscosity in glass-forming metallic liquids*

Momentum transport in the context of shear viscosity can be equally revealing to the mass transport problem discussed above in understanding glass-forming metallic liquids, at the level of atomic processes, structure and forces. It is then not surprising that some emphasis has been placed on the HS model. Notable work on the one-component case is that of Longuet-Higgins and Pople [35] and Collins and Raffel [36]. These authors obtain the shear viscosity for this model in the approximate form

$$\eta = \frac{2\sigma^2}{15}\left(\frac{Mk_{\mathrm{B}}T}{\pi}\right)^{1/2} g(\sigma), \tag{15}$$

where M is the mass of the HS having a diameter σ, and $g(\sigma)$ is the value of the pair correlation function. We note here that, by using computations by Speedy [37] and by Erpenbeck and Wood [38] on diffusion in the HS model, Angilella *et al.* [39] have recently proposed a refinement of the analytic form of Equation (15).

Turning to the two-component model, we next note that Faber [40] and Singh and Sommer [41] have written a generalisation of Equation (15) in terms of the partial pair correlation functions $g_{ij}(r)$ for HS of diameters σ_A and σ_B in the AB alloy. This takes the form:

$$\eta = \frac{4}{15}(\pi k_{\mathrm{B}}T)^{1/2}\rho^2 \sum_i \sum_j c_i c_j (m_j)^{1/2}\left(\frac{\sigma_i+\sigma_j}{2}\right)^4 g_{ij}\left(\frac{\sigma_i+\sigma_j}{2}\right), (i,j = A, B), \tag{16}$$

where m_j are the atomic masses and ρ is the average density. However, it is found [41] that Equation (16) does not work for the systems Bi–Ga and Bi–Zn. In Section 2, Ga was shown to be definitely non-HS-like. We should add here that for pure liquid Bi near melting, the long-wavelength limit of the structure factor, $S(q=0)$, is known to be 0.0093, and hence the argument of Bernasconi and March [2] clearly points to Bi also being non-HS-like. Thus, it is quite possible that Equation (16) will prove useful in practice when both elements in the binary liquid alloy satisfy the necessary conditions set out in Section 2 for HS-like behaviour.

Let us turn from the HS model to the phenomenological treatment of the shear viscosity in glass-forming metallic liquids. Then it is noteworthy that in work done almost six decades ago, Doolittle [42] related η to the available free volume $\Omega - \Omega_0$ [43] by writing

$$\eta = A \exp\left(\frac{b\Omega_0}{\Omega - \Omega_0}\right), \tag{17}$$

where Ω_0 is the volume per atom. However, we prefer here to stress the more basic phenomenology going back to the study of Adam and Gibbs [5]. Utilising explicitly Equations (21) and (22) of their paper we are then led to write the shear viscosity η in the form

$$\eta = B \exp\left(\frac{C}{TS_c}\right), \tag{18}$$

where S_c is the configurational entropy of the glass-forming liquid. Goldstein [44] raised an early objection to putting emphasis on the configurational entropy S_c as a basic variable governing glass formation. However the presence of TS_c in this equation appears to overcome this criticism.

To conclude the discussion on transport we shall next introduce possible generalisations of the SER, well known to be extremely valuable in relating diffusion and shear viscosity in one-component dense liquids to multicomponent glass-forming metallic liquids.

5.3. *Generalisation of the SER for multicomponent glass-forming metallic liquids*

Before turning to multicomponent systems, it is relevant to note that fairly recently there has been interest in the SER in some pure liquid metals [45–47]. In its simplest formulation, the SER states that the diffusion coefficient D of a particle of radius R immersed in a fluid with viscosity η is given by $D = k_B T / 6\pi\eta R$. Generally speaking, in these studies the validity of the SER, relating D and η, was accepted in semi-quantitative terms and the focus was therefore to explain relatively modest departures from it.

As to the relevance of the SER to multicomponent glass-forming metallic liquids, we shall focus first on the experimental studies of Meyer [48] and Meyer *et al.* [49]. Specifically, liquid $Pd_{43}Ni_{10}Cu_{27}P_{20}$ has been investigated by Meyer [48] using incoherent inelastic neutron scattering. As Meyer stresses, this material is characterised by a dense packing, corresponding to a packing fraction greater than 0.5. Also it is known that at the above composition, a cooling rate as low as $0.09\,\mathrm{K\,s^{-1}}$ is sufficient to prevent crystallization and to form a bulk metallic glass [50]. Meyer concludes that diffusivities derived from mean relaxation times compare favourably with Co diffusivities from tracer diffusion measurements. And most importantly in the present context, diffusivities calculated from viscosity via the SER also compare well. Unfortunately, Meyer *et al.* [20] have subsequently investigated atomic transport in ZrTiCuNiBe melts, with quite a different conclusion in relation to the SER. Both $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ and $Zr_{46.8}Ti_{8.2}Cu_{7.5}Ni_{10}Be_{27.5}$ melts were investigated. Again by means of incoherent, quasi-elastic neutron scattering, Meyer and coworkers could extract an average self-diffusion coefficient of the incoherent scatterers Ni and Ti. The viscosity data of Masuhr *et al.* [51] was used in the context of the SER. In contrast to the findings on liquid PdNiCuP alloys summarised above, the mean Ni and Ti self-diffusivity (for PdNiCuP, Ni and Cu) could not be usefully expressed in terms of the measured shear viscosity by means of the SER.

Das *et al.* [52] have used both inelastic neutron scattering and molecular dynamics (MD) to study the influence of chemical short-range order on atomic diffusion in Al–Ni melts. The temperature and concentration dependence of the measured diffusion coefficients are reproduced satisfactorily by their MD simulations. Again the conclusion here is that transport is strongly influenced by packing effects, even though the interatomic forces depend strongly on chemical short-range order. It would be of interest in the future if measurements plus MD simulations of shear viscosity could be obtained, to assess whether the SER is useful for this binary metallic alloy.

Having reviewed briefly experimental neutron scattering results on the binary metallic liquid Al–Ni, we now want to lay down a route by which, in the long term, relations between transport coefficients may emerge from first-principles theory. We take as starting point the theoretical study of Bhatia *et al.* [53]. In their work they introduced the so-called M–X dynamical structure factors, which are essentially the FT of the mass-density and mass-concentration correlation functions. As will be demonstrated below, these M–X structure factors are intimately related to transport in binary metallic liquids.

Let us consider, specifically, a binary metallic liquid within a volume V having $N_\alpha (\alpha = 1, 2)$ atoms of type α which contribute a mass M_α to the total mass $M(=M_1 + M_2)$ of all $N(=N_1 + N_2)$ atoms in the alloy. If $\rho_\alpha = M_\alpha / V$ is the mean mass-density of the α species, then we define the mean mass-concentration, x say, by:

$$x = M_1/M = \rho_1/\rho, \tag{19}$$

where $\rho = M/V$ is the mean mass-density. Also it is helpful to define the mean number concentration as $c = N_1/N$. We shall denote the local mass-density at time t and position $\mathbf{r}$ for species α by $\rho_\alpha(\mathbf{r}, t)$, and then we write the local fluctuation $\delta\rho_\alpha(\mathbf{r}, t)$ in this quantity as:

$$\delta\rho_\alpha(\mathbf{r}, t) = \rho_\alpha(\mathbf{r}, t) - \rho_\alpha = m_\alpha \delta n_\alpha(\mathbf{r}, t). \tag{20}$$

Evidently $\delta n_\alpha(\mathbf{r}, t)$ here is the fluctuation in the local number–density operator of species α. Also in Equation (20), m_α is the molar mass, per atom, of species α, $m_\alpha = M_\alpha / N_\alpha$. We next form the local fluctuations in the total mass-density and mass-concentration, respectively, as:

$$\delta\rho(\mathbf{r}, t) = \delta\rho_1(\mathbf{r}, t) + \delta\rho_2(\mathbf{r}, t) \tag{21}$$

and

$$\delta x(\mathbf{r}, t) = \rho^{-1}[(1 - x)\delta\rho_1(\mathbf{r}, t) - x\delta\rho_2(\mathbf{r}, t)]. \tag{22}$$

Writing the following Fourier expansions:

$$\delta\rho(\mathbf{r}, t) = V^{-1} \sum_{\mathbf{q}} M(\mathbf{q}, t) e^{-i\mathbf{qr}} \tag{23}$$

and

$$\delta x(\mathbf{r}, t) = \sum_{\mathbf{q}} X(\mathbf{q}, t) e^{-i\mathbf{qr}}, \tag{24}$$

we find

$$M(\mathbf{q}, t) = M^{+}(-\mathbf{q}, t) = \int e^{i\mathbf{qr}} \delta\rho(\mathbf{r}, t) \mathrm{d}\mathbf{r} \tag{25}$$

and

$$X(\mathbf{q},t)=X^{+}(-\mathbf{q},t)=V^{-1}\int e^{i\mathbf{qr}}\delta x(\mathbf{r},t)\mathrm{d}\mathbf{r}. \tag{26}$$

This then leads to the desired *M*–*X* dynamical structure factors as:

$$S_{MM}(\mathbf{q},\omega)=\frac{1}{2\pi M}\int e^{-i\omega t}\langle M^{+}(\mathbf{q},0)M(\mathbf{q},t)\rangle\mathrm{d}t, \tag{27}$$

$$S_{MX}(\mathbf{q},\omega)=\frac{1}{4\pi}\int e^{-i\omega t}\langle M^{+}(\mathbf{q},0)X(\mathbf{q},t)X^{+}(\mathbf{q},0)M(\mathbf{q},t)\rangle\mathrm{d}t, \tag{28}$$

$$S_{XX}(\mathbf{q},\omega)=\frac{M}{2\pi}\int e^{-i\omega t}\langle X^{+}(\mathbf{q},0)X(\mathbf{q},t)\rangle\mathrm{d}t, \tag{29}$$

where $\langle\cdots\rangle$ denotes the ensemble average. These are the appropriate dynamical structure factors from which to forge intimate links with the transport coefficients in a binary metallic liquid. One can proceed to form Kubo–Green-like formulae, and indeed the first one involving $S_{MM}(\mathbf{q},0)$ parallels completely the one-component case by yielding the combination of shear viscosity η and its bulk viscosity [3] counterpart χ as

$$\lim_{\omega\to 0}\omega^{4}\lim_{q\to 0}\frac{1}{q^{4}}S_{MM}(\mathbf{q},\omega)=\frac{k_{\mathrm{B}}T}{\pi\rho}\left(\frac{4}{3}\eta+\chi\right). \tag{30}$$

$S_{XX}(\mathbf{q},\omega)$, on the other hand, involves the coefficient of mutual diffusion, D_{12} say, through

$$\lim_{\omega\to 0}\omega^{2}\lim_{q\to 0}\frac{1}{q^{2}}S_{XX}(\mathbf{q},\omega)=\frac{Mk_{\mathrm{B}}T}{\pi}\frac{D_{12}}{Z_{X}}, \tag{31}$$

where Z_X is a thermodynamic quantity derivable from the Gibbs free energy of the binary liquid as

$$Z_{X}=\left(\frac{\partial^{2}G}{\partial x^{2}}\right)_{P,T,M}. \tag{32}$$

The cross relation involving $S_{MX}(\mathbf{q},\omega)$ is more complex, involving D_{12} again, but we shall not take it further here. Through Equations (30) and (31) it would seem to be a clear objective for future study, to forge a link, albeit approximate, between the viscosity combination $(4\eta/3+\chi)$ and the coefficient of mutual diffusion D_{12}, the thermodynamic quantity Z_X being also involved.

6. Discussion and proposed future directions

Motivated by the study of Chathoth *et al.* [1], we have focused here on the issue of when possible HS-like behaviour will be in evidence in multi-component glass-forming metallic liquids. It seemed natural to begin the discussion with pure liquid metals. Table 1, obtained from thermodynamic data plus diffraction measurements on 15 liquid metals near freezing [2], showed in the final column a ratio which must be near to unity as a necessary condition for HS behaviour. Combined with subsequent data by Krishnan and Price [12] from levitation plus diffraction studies, one has 10 of the 15 pure liquid metals in Table 1 as satisfying the necessary condition to be HS. The three polyvalent metals Ga, Pb and Sn are, however, thereby excluded. Less decisively, the two remaining candidates in Table 1, namely Cs and Co, should presently, we believe, be excluded from the HS category. From [12] Zr is possibly in the HS category, whereas it has been argued from experimental thermodynamic data that Bi is definitely non-HS. Finally, Be from the electron theory study of Perrot and March [22] is also to be viewed as non-HS.

Returning to the study of Chathoth *et al.* [1], the binary liquid metallic alloy NiNb qualifies as possibly HS-like. In the NiNbSn melts, Sn is in the non-HS category. As mentioned above, at low concentrations of Sn this is unlikely to alter the dominance of the packing fraction; substantial increase in the Sn concentration, if that proves possible experimentally, may lead to important interplay between packing fraction effects and characteristic metallic tails, in which a repulsive region follows the principal minimum in an (assumed) pair potential description. Similar comments apply to the ZrTiNiCuBe alloys. The concentration of Be, between 20 and 30% in these alloys, means that interplay between HS behaviour and metallic-like tails may be important here. The final example is the metallic glass $W_{60}Ir_{20}B_{20}$ cited by Greer [23]. Liquid B is known from [12] to be metallic, and non-HS behaviour can safely be anticipated for the above alloy, because of the chemical bonding propensities of B.

Turning to transport properties, but now more briefly because they will be an important element in proposals to be made below, the HS Equation (16) is found not to work for the shear viscosities in the binary metallic liquid systems Bi–Ga and Bi–Zn, both Bi and Ga having been identified in the present study as non-HS. As the final point before turning to proposals for the future, general consensus is now emerging that in multicomponent glass-forming metallic liquids the glass transition must be characterised by cooperative motion of numerous atoms. This is reflected, for example, in the early and basic phenomenology of Adam and Gibbs [5], which leads to a relation of the form of Equation (18) between shear viscosity and TS_c, where S_c is the configurational entropy.

As to further directions for research in the area of the present study, which has, of course, importance both for basic science and for technological applications, there is an important balance to preserve. As to the former, we think that the basic theory of the M–X dynamical structure factors, set out in Section 5.3 in relation to neutron scattering and momentum and mass transport coefficients, is a pointer towards relating mutual diffusion (see Equation (31)) and a combination of shear plus bulk viscosity (see, for instance, Equation (30)) in binary glass-forming metallic liquids. We stress this because more straightforward attempts to construct generalisations of the one-component SER have only had modest success to date, with numerous counterexamples known. The work of Faupel *et al.* [28] points to an important experimental route relating to the above proposals.

Returning to theoretical models, we have not referred before in the present article to mode-coupling theory. There are at least two reasons for this. The first is because this area has been covered in its entirety in a recent book by Gotze [54]. Second, as stressed by Zacarelli *et al.* [55] in the framework of colloids, the precise delineation of the regime of applicability of mode-coupling theory concepts remains to be clarified.

In gaining further structural insight, we believe that reverse Monte Carlo studies [56] are noteworthy contributions to this general area of glass-forming multicomponent metallic liquids [57], and point to another important direction for future studies.

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