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LETTER TO THE EDITOR

The solute triplet partial structure factor in the long-wavelength limit of highly diluted liquid binary alloys—application to liquid mercury alloys with the minimum in the thermoelectric power Q

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Abstract. A new solute triplet partial structure factor (STPSF) in the long-wavelength (LWL) limit for highly diluted liquid binary alloys, $K_{111}(0, 0)$, is presented on the basis of the formulation of Parrinello and Tosi. This new STPSF in the LWL limit can be evaluated by using classical thermodynamic parameters such as an interaction parameter ϵ_{11} and a size factor δ_0 . Numerical calculations of this $K_{111}(0, 0)$ have been made for liquid mercury alloys with a minimum in the thermoelectric power Q . The degree of the minimum in the thermoelectric power Q increases with the increase of the magnitude of this $K_{111}(0, 0)$. This fact also indicates the importance of higher-order correlation effects for the origin of the minimum in the thermoelectric power Q , which has been pointed out in recent studies by Itami and co-workers.

Recently it has been found that local structural effects are responsible for particular properties of some liquid alloys. For example, electrical resistivities of liquid alkali–Pb alloys show sharp maxima at specific stoichiometric compositions, such as the composition of Li_4Pb (Nguyen and Enderby 1977) and KPb (Meijer *et al* 1985). Such features of liquid alkali–polyvalent alloys are sometimes called as ‘chemical short-range order’ effects.

For a substantial understanding of this kind of effect, it is very important to clarify the behaviour of higher-order correlation functions in addition to pair correlation functions both experimentally and theoretically. In particular, for some liquid mercury-based alloys a curious minimum in the thermoelectric power Q has been found on the isothermal concentration dependence curve of Q (see, for example, Itami *et al* 1982, 1983, 1984). It has been concluded that the minimum in Q is caused by anomalous behaviour of the higher-order correlation function between ionic configurations. Therefore, the higher-order correlation function of mercury alloys was studied directly by an experimental method. Unfortunately, however, information on pair correlation functions is directly obtained by conventional experimental methods of structure analyses, such as x-ray or neutron diffraction experiments. Information on the higher-order correlation function can only be extracted indirectly from the temperature or pressure derivative of pair

correlation functions obtained directly by these experiments. At present, computer simulations and EXAFS, which are suitable for the study of the higher-order correlation function of liquids, are not always available for liquid Hg alloys because of the lack of information about the ionic interactions or complicated methods of analyses. Therefore, it is very interesting to study the behaviour of the higher-order correlation function of these liquid Hg alloys from a theoretical point of view. Parrinello and Tosi (1975) and Bhatia and Ratti (1976a, b) presented the formulations of triplet correlations functions or triplet partial structure factors of liquid mixtures. We propose here a new form of a solute triplet partial structure factor (STPSF) in the long-wavelength (LWL) limit appropriate to highly diluted liquid alloys; this discussion is based on the formulation of Parrinello and Tosi (1975). Numerical calculations are performed in the case of liquid Hg alloys with the minimum in Q and this minimum in Q is discussed from the point of view of STPSF in the LWL limit.

According to Parrinello and Tosi (1975), the triplet partial structure factor of cluster type (Uhlenbeck and Ford 1962), $T_{ijk}(0, q)$, is related to both the concentration derivative and the density derivative of the partial structure factor, $S_j(q)$, of the type described in Ashcroft and Langreth (1967). This is essentially based on the fact that derivatives of the pair correlation function, $g_{ij}(r)$, such as density, concentration and temperature derivatives of $g_{ij}(r)$, generate the integrated higher-order correlation function in addition to the pair correlation function itself (Kirkwood and Buff 1951, Buff and Brout 1955, Schofield 1966). Therefore, in principle, the integrated triplet correlation function can be expressed by these derivatives (Parrinello and Tosi 1975, Bhatia and Ratti 1976a, b).

Particularly in the LWL limit ($q \rightarrow 0$), this integrated triplet correlation function corresponds to the triplet partial structure factor in the LWL limit, $T_{ijk}(0, 0)$. In the case of a binary mixture, the STPSF in the LWL limit of Parrinello and Tosi (1975), $T_{111}(0, 0)$, can be written as follows:

$$T_{111}(0, 0) = (C\rho)^2 \int [g_{111}(\mathbb{R}_1, \mathbb{R}_2, \mathbb{R}_3) - g_{11}(\mathbb{R}_1, \mathbb{R}_2) - g_{11}(\mathbb{R}_2, \mathbb{R}_3) - g_{11}(\mathbb{R}_3, \mathbb{R}_1) + 2] d(\mathbb{R}_1 - \mathbb{R}_2) d(\mathbb{R}_1 - \mathbb{R}_3) \quad (1)$$

$$T_{111}(0, 0) = (CS_{NN}(0) + S_{NC}(0))\rho(\partial S_{11}(0)/\partial\rho)_{T,C} + \rho v_2 S_{CC}(0)(\partial S_{11}(0)/\partial C)_{T,\rho} - (2 - (\rho v_2/C)S_{CC}(0) - CS_{NN}(0) - S_{NC}(0))(S_{11}(0) - 1). \quad (1')$$

In equation (1), $g_{111}(\mathbb{R}_1, \mathbb{R}_2, \mathbb{R}_3)$ is the triplet correlation function between solute species and \mathbb{R}_i is the position vector of the i th particle; $g_{11}(\mathbb{R}_1, \mathbb{R}_2)$ is the pair correlation function between solute species and is equal to $g_{11}(r_{12})$ as a function of r_{12} ($\equiv |\mathbb{R}_1 - \mathbb{R}_2|$) only. In equation (1'), the subscript 1 indicates the solute species (and subscript 2 the solvent species); C is the concentration of the solute; ρ is the number density; v_i is the partial molar volume of component i per one particle; $S_{NN}(0)$, $S_{NC}(0)$ and $S_{CC}(0)$ respectively the number–number, number–concentration, and concentration–concentration correlation function in the LWL limit presented by Bhatia and Thornton (1970). Here we define the new STPSF in the LWL limit, $K_{111}(0, 0)$, which is appropriate to the dilute concentration range of binary mixtures, as follows:

$$K_{111}(0, 0) \equiv T_{111}(0, 0)/C^2 \quad (2)$$

$$K_{111}(0, 0) = \rho(S_{NN}(0) + S_{NC}(0)/C)(\partial a_{11}(0)/\partial\rho)_{T,C} + \rho v_2(S_{CC}(0)/C)(\partial a_{11}(0)/\partial C)_{T,\rho} - [2/C - (2\rho v_2/C^2)S_{CC}(0) - S_{NN}(0) - S_{NC}(0)/C](a_{11}(0) - 1). \quad (2')$$

In equation (2'), partial structure factors of the type used by Faber and Ziman (1965), $a_{ij}(0)$, were employed rather than those of Ashcroft and Langreth (1967), $S_{ij}(0)$. In principle all quantities in equation (2'), which corresponds to the expression of the thermodynamic limit, can be expressed by the usual macroscopic thermodynamic quantities, such as the compressibility κ_T , the thermal expansion coefficient α_T , the size factor δ_0 , the interaction parameter ε_{11} , etc.

As was done by Favre-Bonte and Desre (1980a,b)†, particularly in the case of extremely dilute liquid alloys (in the limit $C \rightarrow 0$) with strong chemical interactions (large ε_{11}), equation (2') becomes approximately a very simple form, as follows:

$$K_{111}(0, 0) \approx 2\varepsilon_{11}^2 + (5\delta_0 + 2)\varepsilon_{11}. \quad (3)$$

In this equation ε_{11} is the so-called Wagner's interaction parameter (Wagner 1952) defined as $\varepsilon_{11} \equiv (\partial \ln \gamma_1 / \partial C)_{C \rightarrow 0}$, where γ_1 is the activity coefficient of component 1 (solute); δ_0 is the so-called size factor in the dilute limit ($C \rightarrow 0$) defined by $\delta_0 \equiv (\partial v / \partial C)_{C \rightarrow 0} / v_2$, where v is the atomic volume ($v = Cv_1 + (1 - C)v_2$) and v_i is the partial molar volume of component i .

The accuracy of this simplified equation (3) can be estimated by using typical values of these thermodynamic coefficients (see Favre-Bonte and Desre 1980a, b); estimated errors are very small for dilute liquid alloys with strong chemical interactions (large ε_{11}), for example, below 1% for $\varepsilon_{11} \geq 6$ and below 4% even for the case of $\varepsilon_{11} \geq 3$.

The practical applications of equation (2') were made for the case of liquid Hg-based alloys, which are known to be interesting systems showing a very curious phenomenon, a minimum in the thermoelectric power Q . Estimations of the ε_{11} , required for an evaluation of the $K_{111}(0, 0)$, were made by using the selected values of the Gibbs free energy of liquid Hg alloys at 298 K compiled by Hultgren *et al* (1973).

The values of δ_0 were estimated from the density measurements by Morikawa *et al* (1987) for liquid Hg-Na, by Kitajima *et al* (1974) for liquid Hg-K, by Sato *et al* (1982) for liquid Hg-Cs and Hg-Tl, and by Morikawa *et al* (1986) for liquid Hg-In. Unfortunately, there is no experimental data available for the density for liquid Hg-Li alloys. Therefore, the value of δ_0 for liquid Hg-Li alloys was estimated by using an approximate formula, $\delta_0 \approx (v_{\text{Li}}^0 - v_{\text{Hg}}^0) / v_{\text{Hg}}^0$, where v_{Li}^0 and v_{Hg}^0 are respectively the atomic volume of liquid Li and that of liquid Hg in the respective pure state (Lucas 1984). As described below, the evaluated values of $K_{111}(0, 0)$ are dominated by the values of ε_{11} and they are insensitive to the assumption for the estimation of δ_0 .

In order to investigate the temperature dependence of $K_{111}(0, 0)$, estimations of ε_{11} at 298, 348, 398 and 448 K were also made for liquid Hg alloys containing Na, for which accurate EMF measurements have recently been performed as a detailed function of the temperature and the solute Na concentration by Morikawa *et al* (1989).

The parameters employed for the evaluation of $K_{111}(0, 0)$ are shown in table 1 together with $K_{111}(0, 0)$ itself and the activity coefficient of the solute in the infinite dilution, γ_1^0 .

Figure 1 shows the temperature dependence of $K_{111}(0, 0)$ for liquid Hg-based alloys containing Na as a solute. As expected, $K_{111}(0, 0)$ is a decreasing function of temperature. For comparison, the values of $K_{111}(0, 0)$ at 298 K for other various liquid Hg-based alloys are also shown in this figure. The magnitude of $K_{111}(0, 0)$ of liquid Hg alloys depends on the solute species such as In, Tl, Li, Na, K and Cs element; the smallest $K_{111}(0, 0)$ is obtained in the case containing In as a solute, and the replacement of In by other solute

† The first term in $(\partial a_{11}(0) / \partial C)_{T,p}$ on p 192 in the paper of Favre-Bonte and Desre (1980a) should be removed.

Table 1. The solute triplet partial structure factor, $K_{111}(0, 0)$ and related thermodynamic parameters (see the text). Density data required for estimations of δ_0 should be referred to the text.

Solute	T (K)	$\ln \gamma_1^0$	ϵ_{11}	δ_0	$\log_{10} K_{111}(0, 0)$
Li	298	-33.3	35.3 ^a	-0.1	3.41
Na	298	-29.7	36.2 ^{a,b}	-0.08	3.43
	348	-24.3	34.0 ^b	-0.08	3.36
	398	-21.2	32.0 ^b	-0.08	3.32
	448	-18.4	28.9 ^b	-0.08	3.23
K	298	-37.3	72.5 ^a	0.75	4.04
Cs	298	-34.6	95.2 ^a	1.46	4.28
In	298	-3.52	7.3 ^a	0.0	2.08
Tl	298	-2.13	12.4 ^a	0.15	2.53

^a Hultgren *et al* (1973).

^b Morikawa *et al* (1989).

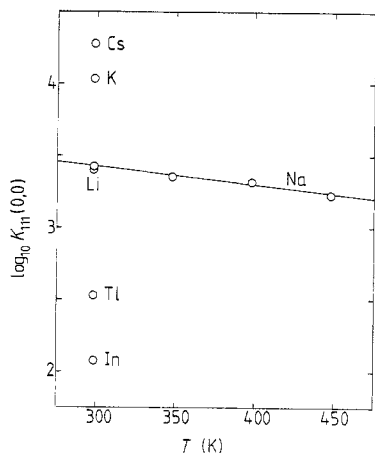


Figure 1. The temperature dependence of the logarithm of the solute triplet partial structure factor in the long-wavelength limit, $\log_{10} K_{111}(0, 0)$. The data are plotted for various liquid Hg-based alloys containing the respective solute element indicated in this figure.

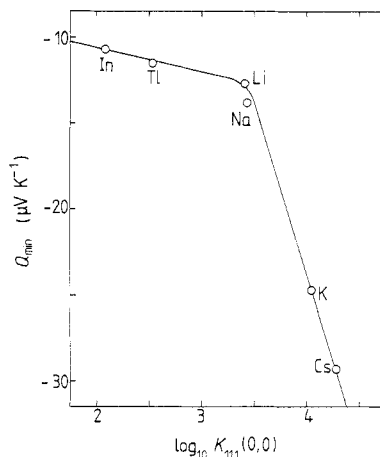


Figure 2. The relation between the value of the minimum in the thermoelectric power Q_{\min} , and the logarithm of the solute triplet partial structure factor in the long-wavelength limit, $\log_{10} K_{111}(0, 0)$. The data are plotted for various liquid Hg-based alloys containing the respective solute element indicated in this figure.

elements makes the $K_{111}(0, 0)$ greater in the order of solute species given above; the largest $K_{111}(0, 0)$ is obtained for the alloy containing Cs as a solute.

The value of ϵ_{11} at 298 K of liquid Hg–Na alloys was estimated from the two different data sources of Gibbs free energy; these are the selected values by Hultgren *et al* (1973) and the recent EMF data by Morikawa *et al* (1989). The same value of ϵ_{11} , 36.2, was obtained using either of these two different data sources. This indicates that the resultant errors of estimations of the ϵ_{11} and the $K_{111}(0, 0)$ are not so large. Here we note that the values of ϵ_{11} for liquid Hg alloys ($\epsilon_{11} \approx 7$ –95) are larger than those of other alkali

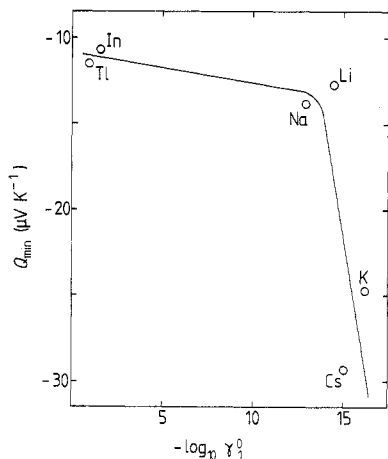


Figure 3. The relation between the value of the minimum in the thermoelectric power Q , Q_{\min} , and the logarithm of the activity coefficient of solute species in the infinite dilution multiplied by -1 , $-\log_{10} \gamma_1^0$. The data are plotted for various liquid Hg-based alloys containing the respective solute element indicated in this figure.

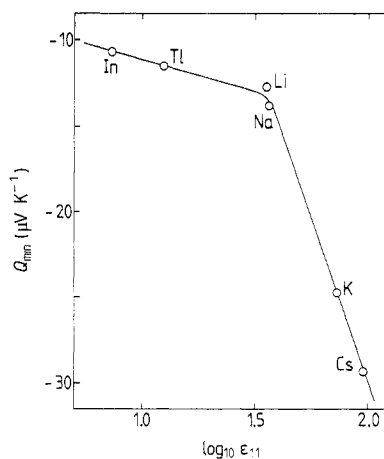


Figure 4. The relation between the value of the minimum in the thermoelectric power Q , Q_{\min} , and the logarithm of the interaction parameter ϵ_{11} , $\log_{10} \epsilon_{11}$. The data are plotted for various liquid Hg-based alloys containing the respective solute element indicated in this figure.

polyvalent alloys containing an alkali element as a solute. Saboungi and co-workers recently presented data for ϵ_{11} of liquid alkali polyvalent alloys containing an alkali element as a solute. Typical examples are as follows: $\epsilon_{11} = 2.2$ for liquid Bi–Na alloys at 673 K and $\epsilon_{11} = 0.65$ for liquid Sn–Na alloys at 573 K (Saboungi and Corbin 1984), $\epsilon_{11} = 3.6$ for liquid Pb–Na alloys at 723 K (Saboungi *et al* 1985), $\epsilon_{11} = 3.3$ for liquid Bi–K alloys at 873 K (Petric *et al* 1988). As can be seen from equation (3), $K_{111}(0, 0)$ is an increasing function of ϵ_{11} for positive ϵ_{11} and positive δ_0 , which are expected for these alkali polyvalent alloys. Therefore, $K_{111}(0, 0)$, which represents the degree of the higher-order correlation between solute species, in liquid Hg-based alloys may be larger than that in other liquid polyvalent-based alloys containing an alkali element as a solute.

We report in figure 2 the value of the minimum in the thermoelectric power Q , determined experimentally, versus $\log_{10} K_{111}(0, 0)$ for the Hg alloys considered. The value of the minimum in Q , Q_{\min} , decreases and the degree of the minimum in Q increases with the increase of the new STPSF in the LWL limit $K_{111}(0, 0)$. Here values of Q_{\min} were quoted from the reference by Fielder (1967) for the liquid Hg–In and –Na systems at 500 K, by Itami and Shimoji (1973) for the liquid Hg–K system at 523 K, by Itami *et al* (1982) for the liquid Hg–Tl system at 500 K and the liquid Hg–Cs system at 523 K, and by Itami *et al* (1984) for the liquid Hg–Li system at 473 K. Small differences in temperature corresponding to the quoted values of Q_{\min} were neglected here by taking into account accuracies of measurements of the thermoelectric power Q . In addition, comparisons were made between $K_{111}(0, 0)$ at 298 K and Q_{\min} near 500 K; too many extrapolation procedures, required for obtaining Q_{\min} at 298 K or $K_{111}(0, 0)$ at 500 K, were avoided in this study.

As displayed in figure 3, the correlation between Q_{\min} and $-\log_{10} \gamma_1^0$ is less than the correlation between Q_{\min} and $K_{111}(0, 0)$. As a gross feature a decreasing tendency of the

value of Q_{\min} (an increasing tendency of the degree of the minimum in Q) can be seen with the increase of $-\log_{10}\gamma_1^0$. However, the value of $-\log_{10}\gamma_1^0$ in the case of solute K is larger than that in the case of solute Cs in spite of the fact that the degree of Q_{\min} in the former case is distinctly smaller than that in the latter case.

Figure 4 shows the dependence of Q_{\min} on $\log_{10}\epsilon_{11}$. This curve is quite similar to that of $\log_{10}K_{111}(0, 0)$. As expected from the form of relation (3), this indicates that the value of the ϵ_{11} contributes dominantly to the evaluation of $K_{111}(0, 0)$ for such liquid Hg alloys with positively large values of the $\epsilon_{11}(>7)$.

In this Letter we attempted to extract information on the triplet correlation from experimental thermodynamic coefficients by using the simple formula (3) based on the theory of Parrinello and Tosi (1975), who made numerical calculations of the triplet correlation function of cluster type (Uhlenbeck and Ford 1962) for liquid Na–K alloys. On the other hand, Bhatia and Ratti (1976a, b) discussed this triplet correlation of liquid Na–K alloys in a somewhat different manner by using number–concentration correlation functions of the type used by Bhatia and Thornton (1970). A similar approach was applied to liquid K–Cs and Na–Cs alloys by Gallego *et al* (1987). However, these discussions are based on the assumption of the conformal solution theory. Unfortunately this assumption is not appropriate for liquid Hg alloys, particularly for liquid Hg alloys containing alkali elements, as can be seen in the thermodynamic data of these alloys (Hultgren *et al* 1973, Ishiguro *et al* 1982, Morikawa *et al* 1989).

Favre-Bonte and Desre (1980a, b) presented an expression of the triplet partial structure factor between solute species in the LWL limit, which should be applied to extremely dilute liquid alloys. They tried to decouple the triplet partial structure factor of cluster type into the purely triplet partial structure factor and the doublet one. However, as a matter of fact, this procedure introduces a divergence problem of the purely triplet partial structure factor, as can be seen from the fact that the V_m in the right-hand side of equation (3) of Favre-Bonte and Desre (1980a, b) should be considered to be the volume of the whole system of interest, which in principle can be infinitely large. As described above, the present status of theoretical research for higher-order correlation functions of liquid alloys is insufficient. Therefore, it is strongly desirable to develop theoretical research in this field. In this study, it has been confirmed that the origin of the minimum in Q may be derived from effects of the higher-order correlation function with the evidence of good correlation between the Q_{\min} and the new solute triplet partial structure factor, $K_{111}(0, 0)$, though the establishment of the microscopic picture remains an interesting future problem.

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