Excess Entropy, Diffusion Coefficient, Viscosity Coefficient and Surface Tension of Liquid Simple Metals from Diffraction Data

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In this paper, we will provide a prescription for evaluating properties of liquid metals from measured diffraction data. When a liquid metal structure factor is of hard-sphere form, there is a correlation between structure factor and entropy. This is investigated for liquid alkali, noble and typical polyvalent metals. First of all, we calculate the pair and triplet correlation entropies \( S^{(2)} \) and \( S^{(3)} \) from the measured diffraction data. To evaluate the triplet correlation entropy \( S^{(3)} \), we do not use the superposition approximation of Kirkwood. Next, assuming that the excess entropy (i.e., ion configurational entropy) \( S_E \) is given as \( S^{(2)} + S^{(3)} + S^{(x)} \), where \( S^{(x)} \) denotes an entropy contribution arising from the four-body and higher-order terms of correlations, we calculate the self-diffusion coefficient \( D \) based on Dragutin’s scaling law. By means of \( D \), we estimate the viscosity coefficient \( \eta \) and the surface tension \( \gamma \) for these liquid metals using the Stokes-Einstein relation, the Born-Green equation and Fowler’s formula for the surface tension. We can find there exists a clear relationship between \( S_E \), \( D \), \( \eta \) and \( \gamma \). Predicted values of \( D \), \( \eta \) and \( \gamma \) are reasonable in size in comparison with the available experimental data.

Keywords: excess entropy, diffusion coefficient, viscosity coefficient, surface tension, liquid metals

1. Introduction

An entropy theory of liquids in terms of correlation functions has been revived by Wallace\(^1\)–\(^3\) and generalized by Baranyai and Evans.\(^4\),\(^5\) The theory is based on a systematic expansion of the entropy in terms of the partial \( N \)-particle distribution functions. Using this theory, Yokoyama and coworkers\(^6\),\(^7\) have attempted to estimate the pair and triplet correlation entropies \( S^{(2)} \) and \( S^{(3)} \) of the hard-sphere fluid. From these studies, it turned out that there is no essential difference between the Percus-Yevick (PY)\(^8\),\(^9\) approximation and the generalized mean spherical approximation (GMSA)\(^10\) in the entropy calculations. In these studies, the superposition approximation of Kirkwood\(^11\) was not used for evaluation of \( S^{(3)} \). The reason is that if we use Kirkwood’s approximation the irreducible part of the triplet correlation function \( \delta g^{(3)}(r, s, t) \) becomes unity, which leads to omission of the major term of \( S^{(3)} \) from the beginning (see the first integral of eq. (3) in Section 2 and see also Yokoyama and Arai\(^12\) for more details). Their results are entirely consistent with Monte Carlo simulations performed by Baranyai and Evans\(^13\) over a range of thermodynamic states. This method was first applied to liquid iron, cobalt and nickel\(^14\) over an extended temperature range of approximately 200 K above the melting point.

The purpose of the present paper is to show the entropy calculations of liquid alkali, noble and typical polyvalent metals near the melting point using the formalism given in Refs. 6, 7) and then to estimate the self-diffusion coefficient \( D \), the viscosity coefficient \( \eta \) and the surface tension \( \gamma \) using the result of entropy calculations. To begin with, we have calculated \( S^{(2)} \) and \( S^{(3)} \) using measured diffraction data of Waseda\(^15\) and Waseda and Ueno.\(^16\) Then we evaluate the excess entropy (i.e., ion configurational entropy) \( S_E \) which is given as \( S^{(2)} + S^{(3)} + S^{(x)} \). Here \( S^{(x)} \) denotes an entropy contribution originating from the higher-order expansion terms for \( n \geq 4 \). First, we will estimate the \( S^{(3)} \) using the hard-sphere fluid based on the GMSA theory. Second, we will estimate the \( S^{(x)} \) using the thermodynamic entropy data due to Hultgren \textit{et al.}\(^17\). This paper may be viewed as an extension of the previous work\(^12\) to liquid alkali, noble and typical polyvalent metals. Calculated results of \( S_E \), \( D \), \( \eta \) and \( \gamma \) are compared with the available experimental data.

2. Formalism

2.1 Correlation entropy

We define the ion motional entropy \( S_I \) as follows:

\[
S_I = S_{PG} + S^{(2)} + S^{(3)} + \cdots ,
\]

(1)

where \( S_{PG} \) is the perfect gas entropy, \( S^{(2)} \) the pair correlation entropy, \( S^{(3)} \) the triplet correlation entropy and so on. The correlation entropies are defined by

\[
S^{(2)} = -\frac{1}{2} \rho^2 \int g^{(2)}(r) \ln g^{(2)}(r) dr + \frac{1}{2} \rho \int \left( g^{(2)}(r) - 1 \right) dr ,
\]

(2)

and

\[
S^{(3)} = -\frac{1}{6} \rho^3 \int \int \int \delta g^{(3)}(r, s, t) \ln \delta g^{(3)}(r, s, t) d\rho d\sigma d\tau \\
+ \frac{1}{6} \rho^2 \int \int \left[ g^{(3)}(r, s, t) - g^{(2)}(r) g^{(2)}(s) - g^{(2)}(s) g^{(2)}(t) + g^{(2)}(r) g^{(2)}(t) + g^{(2)}(r) g^{(2)}(s) + g^{(2)}(t) - 1 \right] d\rho d\sigma d\tau ,
\]

(3)

where \( g^{(2)} \) and \( g^{(3)} \) are the pair and triplet correlation functions and \( r = |r| = |r_2 - r_1|, s = |s| = |r_3 - r_1| \) and \( t = |s - r| \). The irreducible part of the triplet correlation function is defined by \( \delta g^{(3)}(r, s, t) = g^{(3)}(r, s, t)/g^{(2)}(r)g^{(2)}(s)g^{(2)}(t) \). Throughout this paper, the entropy is expressed in units of \( k_B \) per particle. The first integral of \( S^{(3)} \) is approximated by (see...
Ref. 6) for details
$$-\frac{1}{6} \rho^2 \int \int \mathbf{g}^{(3)}(r, s, t) \ln \delta \mathbf{g}^{(3)}(r, s, t) dr ds$$
$$\approx -\frac{1}{6} (H_1(0) + H_2(0) + H_3(0)),$$
(4)
where \( H_1(0), H_2(0) \) and \( H_3(0) \) are, respectively, the \( Q = 0 \) values of \( H_1(Q), H_2(Q) \) and \( H_3(Q) \). These functions are given by
$$H_1(Q) = \frac{1}{(2\pi)^3} [S(Q) - 1] * [S(Q) - 1]^2,$$
$$H_2(Q) = [S(Q) - 1][S(0) + S(Q) - 1],$$
(5, 6)
and
$$H_3(Q) = -\rho k_B T \left( \frac{\partial S(Q)}{\partial \rho} \right)_T = -S(0) \rho \left( \frac{\partial S(Q)}{\partial \rho} \right)_T.$$ (7)
In the above equations \( S(Q) \) is the liquid structure factor, and * means the convolution between \([S(Q) - 1]\) and \([S(Q) - 1]^2]\). The second integrals of eqs. (2) and (3) are evaluated by eqs. (20) and (22) of Ref. 6).

2.2 Dzugutov’s scaling law
Recently Dzugutov\(^{18}\) has proposed a scaling law between the excess entropy \( S_e \) and a dimensionless form of the diffusion coefficient \( D^* \), which reads
$$D^* = 0.049 \exp(S_e),$$
(8)
where \( D^* \) is given by
$$D^* = D \Gamma_e^{-1} \sigma^{-2}.$$ (9)
In eq. (9), \( D \) is the diffusion coefficient and \( \Gamma_e \) is the Enskog collision frequency which can be calculated for the temperature \( T \) and the number density \( \rho \)
$$\Gamma_e = 4 \sigma^2 g(\sigma) \rho / (\pi k_B T / m)^{1/2},$$
(10)
where \( m \) and \( \sigma \) are the atomic mass and the hard-sphere diameter. \( g(\sigma) \) represents the value of the pair correlation function \( g(r) \) at the contact distance. In a real system, \( \sigma \) can be interpreted as the position of the first maximum of \( g(r) \). From eqs. (8) and (9), \( D \) is given by
$$D = 0.049 \Gamma_e \sigma^2 \exp(S_e).$$
(11)
In eqs. (8) and (11), Dzugutov has assumed that \( S_e \) can be restricted to the two-particle approximation, i.e., \( S(2) \). However, Yokoyama\(^{10}\) has pointed out that the approximation using \( S(2) \) is not valid and \( S_e \) should be used in these formulae.

2.3 Relationship between diffusion coefficient, viscosity coefficient and surface tension
There is a correlation between the shear viscosity coefficient \( \eta \) and the surface tension \( \gamma \). This correlation has been examined by Egry and coworkers.\(^{20,21}\) Fowler derived a useful formula for the surface tension of a fluid, approximating the smooth density profile by a step function and replacing the gas by vacuum. It reads:
$$\gamma = (\pi \rho^2 / 8) \int_0^\infty drr^4 (du(r)/dr)g(r),$$
(12)
where \( u(r) \) is a pair potential. Very similarly, Born and Green derived an expression for the viscosity of a fluid using kinetic theory. They found
$$\eta = (2\pi \rho^2 / 15)(m / k_B T)^{1/2} \int_0^\infty drr^4 (du(r)/dr)g(r).$$ (13)
Equations (12) and (13) essentially use a hard-sphere model: Fowler’s formula neglects the realistic density profile of finite thickness at the surface, and the Born-Green formula does not contain contributions from the soft, long-range part of the potential. A striking feature of these two expressions is the fact that the two integrals are equal. Therefore, by forming \( \gamma / \eta \), the integral cancels and we obtain
$$\gamma / \eta = (15/16)(k_B T / m)^{1/2}.$$ (14)
Now connecting eq. (14) with the Stokes-Einstein relation with the slipping boundary condition\(^{22,23}\)
$$\eta = k_B T / (2\pi \sigma D),$$
(15)
we obtain
$$\gamma = 15k_B T (k_B T / m)^{1/2} / (32\pi \sigma D).$$ (16)
Since \( D \) is evaluated from eq. (11) in terms of \( S_e, \eta \) and \( \gamma \) are determined from eqs. (15) and (16).

2.4 Evaluation of \( S^{(1)} \) based on both the GMSA theory due to Waisman and the Carnahan-Starling equation of states
To improve the PY approximation at high densities, Waisman\(^{10}\) has chosen a semi-empirical approach to get the pair correlation function \( g^{(3)}(r) \). He has solved the generalized mean spherical approximation (GMSA), where the direct correlation function \( C(r) \) outside the core, which vanishes in the PY theory, is assumed to be given by a Yukawa form. The GMSA due to Waisman agrees closely with Monte Carlo simulations throughout the entire stable fluid phase. In this case, hard-sphere pair correlation functions and hard-sphere structure factors must be used for the entropy calculations. Figure 1 shows comparison of the configurational entropies. The configurational entropy calculated from the Carnahan-Starling(CS)\(^{20}\) equation of states is expressed by
$$\Delta S^{CS} = \xi (3\xi - 4)/(1 - \xi)^2$$
(shown as \( \bigcirc \) in Fig. 1), where


ξ is the packing fraction of the hard-spheres. Our calculated configurational entropy is defined by \( \Delta S^{\text{calc}} = S^{(2)} + S^{(3)} \) (shown as \( \bullet \) in Fig. 1). Solid lines with \( \circ \) and \( \bullet \) are drawn as guides to the eyes. The details of the entropy calculations based on the GMSA theory are well documented in Ref. 7. As seen from Fig. 1, our \( \Delta S^{\text{calc}} \) remains below \( \Delta S^{\text{CS}} \) at intermediate densities up to around \( \xi \approx 0.41 \), but overestimates \( \Delta S^{\text{CS}} \) at greater densities between \( \xi \approx 0.42 \) and 0.47. This means that the four-body and even higher-order terms of correlations have non-negligible contributions, and suggests that \( S^{(k)} \) is evaluated by \( \Delta S^{\text{CS}} - \Delta S^{\text{calc}} \).

3. Results

Numerical results of the entropy calculations are given in Table 1. As seen from Table 1, the average value of \( S^{(3)} \) is about -3.0. We often referred to the entropy analysis given by Wallace.\(^3\) We may regard the value of \( S^{(3)} \approx -3.0 \) as a measure of \( S^{(3)} \) for normal metals. On the other hand, the average value of \( S^{(3)} \) is roughly -1.0. As mentioned in Section 1, \( S^{(3)} \) is given as \( S^{(3)} = S^{(2)} + S^{(3)} + S^{(k)} \), where we evaluated that \( S^{(k)} \approx 0.60 \) near the melting point. The value of 0.60 is determined as follows. The entropy expression based on the hard-sphere packing theory\(^{25}\) is given as

\[
S = S_{\text{HS}} + S_{\xi},
\]

where \( S \) is the total entropy, \( S_{\xi} \) is an entropy contribution arising from the softness of interatomic forces and \( S_{\text{HS}} \) is given by

\[
S_{\text{HS}} = S_{\text{PG}} + S_{\text{PACK}} + S_{\text{elec}}.
\]

Here \( S_{\text{PG}} \) is the perfect gas entropy, \( S_{\text{elec}} \) is the electron-excitation entropy and \( S_{\text{PACK}} \) is the excess entropy due to the finite packing of the hard-spheres, which is best described via the negative Carnahan-Starling expression\(^{25}\), i.e., \( S_{\text{PACK}} = \Delta S^{\text{CS}} = \xi (3 \xi - 4) / (1 - \xi)^2 \). On comparing eq. (17) with eq. (1), since \( S = S_{\xi} + S_{\text{HS}} \), the excess entropy of ion disorder alone \( S_{\xi} \) is given as \( S_{\xi} = S^{(2)} + S^{(3)} + S^{(k)} = S_{\text{PACK}} + S_{\xi} \). Therefore, if we approximate an effective pair interaction between ions by a simple hard-sphere potential (i.e., \( S_{\xi} \to 0 \)), we have \( S^{(2)} + S^{(3)} + S^{(k)} = S_{\text{PACK}} \), so that \( S^{(k)} = S_{\text{PACK}} - (S^{(2)} + S^{(3)}) \). In this case, hard-sphere pair correlation functions and hard-sphere structure factors must be used for the entropy calculations. As mentioned in Subsection 2.4, \( S^{(k)} \) is given as \( \Delta S^{\text{CS}} - \Delta S^{\text{calc}} = \Delta S^{\text{PACK}} - (S^{(2)} + S^{(3)}) \). All entropy calculations can be done by the packing fraction \( \xi \). From the detailed calculations,\(^3\) \( S^{(k)} = -3.94 - (-4.45) = 0.51 \) for \( \xi = 0.450 \) and \( S^{(k)} = -4.15 - (-4.86) = 0.71 \) for \( \xi = 0.461 \) (see also Fig. 1 in the paper). With these values of \( \xi \), as is well known, the experimental structure factor data of liquid metals near the melting point can be well described by the hard-sphere structure factors (see Table 3–1 of Ref. 26) for the liquids concerned in the paper). Hence, we evaluated \( S^{(k)} \) to be 0.60, on an average, near the melting point when a liquid metal structure factor is of hard-sphere form.

The values of \( S_{\xi} \) calculated from the observed diffraction data are in fair agreement with those obtained from the thermodynamic data\(^{17}\) which are also collected in Table 1 for comparison. The way of evaluating the experimental excess entropy \( S_{\xi}(\text{expt}) \) is given in the next section. Predicted values of \( D, \eta \) and \( \gamma \) in terms of \( S_{\xi} \) are summarized in Table 2 and graphically compared in Figs. 2–4 with the experimental data. Our calculated values of \( D, \eta \) and \( \gamma \) are in reasonable agreement with the available experimental data.

4. Discussion

Here we want to deduce \( S^{(k)} \) from the experimental entropy data due to Hultgren et al.\(^{17}\) so as to check the theoretical estimate presented in the previous section. The procedure to be taken for this purpose is as follows. We suppose the experimental excess entropy \( S_{\xi}(\text{expt}) \) is estimated by \( S_{\xi}(\text{expt}) = S_{\text{PG}} - S_{\text{elec}} \), in which \( S_{\text{PG}} \) is the measured total entropy given in the compilation of Hultgren et al. and \( S_{\text{PG}} \) is the perfect gas entropy with \( h \) being the Planck constant

\[
S_{\text{PG}} = \{5/2 + \ln[(1/\rho)(2\pi mk_BT/h^2)^3/2]\}N_{\text{kg}b}, \quad \text{(19)}
\]

and \( S_{\text{elec}} \) is

\[
S_{\text{elec}} = (zT/k_BT)(\pi k_BT/k_F)^2 N_{\text{kg}b}, \quad \text{(20)}
\]

in free electron approximation with \( z, k_F \) being the valency and the Fermi wave number, respectively. Numerical results of both \( S_{\xi}(\text{expt}) \) and \( S^{(k)} \) at various temperatures are summa-
Table 2. $D$, $\eta$ and $\gamma$ of liquid alkali, noble and typical polyvalent metals calculated from the diffraction data.\textsuperscript{15,16}

<table>
<thead>
<tr>
<th>Metal</th>
<th>$T$ (K)</th>
<th>$\sigma$ ($10^{-10}$m)</th>
<th>$g(\sigma)$</th>
<th>$D$ ($10^{-9}$m$^2$·s$^{-1}$)</th>
<th>$\eta$ (mPa·s)</th>
<th>$\gamma$ (Nm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>463</td>
<td>3.0</td>
<td>2.484</td>
<td>6.67</td>
<td>5.98–6.80</td>
<td>0.509</td>
</tr>
<tr>
<td>Na</td>
<td>378</td>
<td>3.7</td>
<td>2.424</td>
<td>3.84</td>
<td>3.85–4.23</td>
<td>0.59</td>
</tr>
<tr>
<td>K</td>
<td>343</td>
<td>4.6</td>
<td>2.351</td>
<td>4.12</td>
<td>3.59–3.76</td>
<td>0.40</td>
</tr>
<tr>
<td>Rb</td>
<td>313</td>
<td>4.8</td>
<td>2.468</td>
<td>2.17</td>
<td>2.22–2.68</td>
<td>0.660</td>
</tr>
<tr>
<td>Cs</td>
<td>303</td>
<td>5.1</td>
<td>2.583</td>
<td>1.84</td>
<td>2.16–2.31</td>
<td>0.709</td>
</tr>
<tr>
<td>Cu</td>
<td>1423</td>
<td>2.5</td>
<td>2.755</td>
<td>3.19</td>
<td>3.18–3.97</td>
<td>3.92</td>
</tr>
<tr>
<td>Mg</td>
<td>953</td>
<td>3.1</td>
<td>2.463</td>
<td>6.85</td>
<td>5.63$^a$</td>
<td>0.986</td>
</tr>
<tr>
<td>Al</td>
<td>943</td>
<td>2.8</td>
<td>2.829</td>
<td>5.07</td>
<td>4.87$^+$</td>
<td>1.46</td>
</tr>
<tr>
<td>Pb</td>
<td>613</td>
<td>3.3</td>
<td>3.073</td>
<td>1.79</td>
<td>1.68–2.19</td>
<td>2.24</td>
</tr>
</tbody>
</table>

$^a$Taken from Refs. 22, 27), $^b$Predicted at 923 K, $^+$Predicted at 933 K.

Fig. 2 Comparison between theory and experiment for $D$ near the melting point. The solid line denotes the 45° axis.

Fig. 3 Comparison between theory and experiment for $\eta$ near the melting point. The solid line denotes the 45° axis.

Fig. 4 Comparison between theory and experiment for $\gamma$ near the melting point. The solid line denotes the 45° axis.

relations. Temperature dependence of the excess entropies is displayed in Figs. 5 and 6 for the demonstrative purposes. For K at 378 K, as Wallace has pointed out in Ref. 3), the value of $S^{(2)}$, hence that of $S^{(x)}$, is apparently inaccurate. Nevertheless, it is clearly seen from the figures that $S^{(2)}+S^{(3)}$ becomes $S_E$ (expt) when the temperature is increased (again except for Pb).

We took no account of experimental errors in $D$, $\eta$ and $\gamma$. In spite of all these uncertainties to be taken into account, we can say that a relationship between the structural, thermodynamic, transport and surface properties of liquid metals emerged from the present entropy calculations.

5. Conclusion

Conclusions drawn from the present work are as follows.

(1) We have calculated $S_E$ of liquid alkali, noble and typical polyvalent metals using the experimental diffraction data. In terms of $S_E$, we have estimated $D$, $\eta$ and $\gamma$. The agreement between theory and experiment for $D$, $\eta$ and $\gamma$ is satisfactory, i.e., it is within 10–20%, which is about the accuracy of the experimental data available at present.

(2) We must admit that the four-body and even higher-order terms of correlations have non-negligible entropy contributions. The estimated value of $S^{(x)}$ is 0.6 (±0.1) near the melting point when a liquid metal structure factor is of hard-
sphere form.

To clarify the relationship between the physical properties of liquid metals, accurate experimental data are highly desirable for $g(r)$, $S(Q)$, $S_E$, $D$, $\eta$ and $\gamma$ at various tempera-

(3) To clarify the relationship between the physical prop-

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\rho$ ($10^3$ kgm$^{-3}$)</th>
<th>$S^{(2)}(N_k)$</th>
<th>$S^{(3)}(N_k)$</th>
<th>$S^{(2)} + S^{(3)}(N_k)$</th>
<th>$S_E(N_k)$</th>
<th>$S^{(3)}(N_k)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na 378</td>
<td>0.926*</td>
<td>−3.06</td>
<td>−1.15</td>
<td>−4.21</td>
<td>−3.46</td>
<td>0.75</td>
</tr>
<tr>
<td>Na 473</td>
<td>0.903*</td>
<td>−2.40</td>
<td>−0.68</td>
<td>−3.08</td>
<td>−2.99</td>
<td>0.09</td>
</tr>
<tr>
<td>Na 573</td>
<td>0.879*</td>
<td>−2.19</td>
<td>−0.60</td>
<td>−2.79</td>
<td>−2.60</td>
<td>0.19</td>
</tr>
<tr>
<td>Na 723</td>
<td>0.844*</td>
<td>−1.83</td>
<td>−0.36</td>
<td>−2.19</td>
<td>−2.20</td>
<td>−0.01</td>
</tr>
<tr>
<td>K 343</td>
<td>0.828*</td>
<td>−2.91</td>
<td>−1.11</td>
<td>−4.02</td>
<td>−3.47</td>
<td>0.55</td>
</tr>
<tr>
<td>K 378</td>
<td>0.819*</td>
<td>−2.44</td>
<td>−0.71</td>
<td>−3.15</td>
<td>−3.27</td>
<td>−0.12</td>
</tr>
<tr>
<td>K 473</td>
<td>0.797*</td>
<td>−2.17</td>
<td>−0.82</td>
<td>−2.99</td>
<td>−2.81</td>
<td>0.18</td>
</tr>
<tr>
<td>K 623</td>
<td>0.762*</td>
<td>−1.83</td>
<td>−0.36</td>
<td>−2.19</td>
<td>−2.29</td>
<td>−0.10</td>
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<tr>
<td>Rb 313</td>
<td>1.479*</td>
<td>−3.08</td>
<td>−1.16</td>
<td>−4.24</td>
<td>−3.59</td>
<td>0.65</td>
</tr>
<tr>
<td>Rb 373</td>
<td>1.460*</td>
<td>−2.67</td>
<td>−0.83</td>
<td>−3.50</td>
<td>−3.16</td>
<td>0.34</td>
</tr>
<tr>
<td>Rb 473</td>
<td>1.419*</td>
<td>−2.12</td>
<td>−0.50</td>
<td>−2.62</td>
<td>−2.65</td>
<td>−0.03</td>
</tr>
<tr>
<td>Cs 303</td>
<td>1.835*</td>
<td>−3.01</td>
<td>−1.22</td>
<td>−4.23</td>
<td>−3.57</td>
<td>0.66</td>
</tr>
<tr>
<td>Cs 373</td>
<td>1.797*</td>
<td>−2.51</td>
<td>−0.81</td>
<td>−3.32</td>
<td>−2.92</td>
<td>0.40</td>
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<tr>
<td>Cs 473</td>
<td>1.740*</td>
<td>−2.00</td>
<td>−0.46</td>
<td>−2.46</td>
<td>−2.36</td>
<td>0.10</td>
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<tr>
<td>Cu 1423</td>
<td>7.97</td>
<td>−3.29</td>
<td>−0.95</td>
<td>−4.24</td>
<td>−3.44</td>
<td>0.80</td>
</tr>
<tr>
<td>Cu 1573</td>
<td>7.86</td>
<td>−2.89</td>
<td>−0.83</td>
<td>−3.72</td>
<td>−3.25</td>
<td>0.47</td>
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<tr>
<td>Cu 1773</td>
<td>7.69</td>
<td>−2.55</td>
<td>−0.60</td>
<td>−3.15</td>
<td>−3.02</td>
<td>0.13</td>
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<tr>
<td>Mg 953</td>
<td>1.545</td>
<td>−2.95</td>
<td>−0.90</td>
<td>−3.85</td>
<td>−3.38</td>
<td>0.51</td>
</tr>
<tr>
<td>Mg 1003</td>
<td>1.433</td>
<td>−2.53</td>
<td>−0.72</td>
<td>−3.25</td>
<td>−3.34</td>
<td>−0.09</td>
</tr>
<tr>
<td>Mg 1153</td>
<td>1.339</td>
<td>−2.33</td>
<td>−0.64</td>
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Fig. 5 Temperature variation of the excess entropy in liquid alkali metals. ●: $S_E$(calc) = $S^{(2)} + S^{(3)}$, × : $S_E$(expt). Error bars are estimated and shown for $S_E$(calc).

Table 3 Correlation entropies at various temperatures and evaluations of $S^{(3)}$ based on the experimental entropy data. \(^{17}\) Densities with * are taken from Wallace, \(^{3}\) others are due to Waseda. \(^{15}\) Although the different densities are often used between Wallace and Waseda, we found that there is no difference in the calculated entropies.
Fig. 6 Same as Fig. 5, but for liquid noble and polyvalent metals.

REFERENCES