Comments on Correlation Entropy Theory by Baranyai and Evans

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The correlation entropy theory by Baranyai and Evans produces non-negligible entropy contributions arising from the four-body and even higher order terms of correlations. If we express this as $S^{(x)}$, the estimated value of $S^{(x)}$ is $0.6 (\pm 0.1) Nk_B$ near the melting point when the structure factor of a liquid metal is of hard-sphere form (I. Yokoyama and S. Tsuchiya: Mater. Trans. **43** (2002) 67–72.). The purpose of the present paper is to propose a way for avoiding the large positive value of $S^{(x)}$ and to show the recalculated results of the total entropy, diffusion coefficient, viscosity coefficient and surface tension of the liquid metals studied in the previous paper using the proposed pair and triplet correlation entropies definitions.

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1. Introduction

Recently Yokoyama and Tsuchiya¹⁾ have presented a paper which provides a prescription for evaluating properties of liquid metals from measured diffraction data. The paper is based on an entropy theory of liquids in terms of correlation functions which has been developed by Baranyai and Evans.^{2,3)} The main conclusions drawn from Ref. 1) are as follows:

- (1) The agreement between the theory and the experiment for diffusion coefficient D , viscosity coefficient η and surface tension γ is satisfactory, *i.e.*, it is within 10–20%, which is about the accuracy of the experimental data available presently.
- (2) The four-body and even higher-order terms of correlations have non-negligible entropy contributions. If we express this as $S^{(x)}$, the estimated value of $S^{(x)}$ is $0.6 (\pm 0.1) Nk_B$ near the melting point when the structure factor of a liquid metal is of hard-sphere form.

In this paper we focus on the latter conclusion. What is the physical meaning of $S^{(x)}$, which has a *rather large positive value*? It is difficult at the moment to give an answer to this question, which is the crucial defect of the correlation entropy theory by Baranyai and Evans. The series expansion of the entropy converges less and less rapidly at high densities than we might have been expected. The trouble originates from the convergence of the series expansion. Our approximations and method of the entropy calculation are not responsible for the cause of the rather large positive value of $S^{(x)}$ (see Table 3 and Fig. 3 of Arai *et al.*⁴⁾).

The purpose of this paper is to propose a way for avoiding the large positive value of $S^{(x)}$, arising from the unfavorable convergence, and to show the recalculated results of the total entropy S_{total} , diffusion coefficient D , viscosity coefficient η and surface tension γ of nine liquid metals studied in Ref. 1) using the proposed pair and triplet correlation entropy definitions.

2. Formalism

As we mentioned in Ref. 1), the ion motional entropy S_I is given by

$$S_I = S_{\text{PG}} + S^{(2)} + S^{(3)} + \dots, \quad (1)$$

where S_{PG} is the perfect gas entropy, $S^{(2)}$ is the pair correlation entropy, $S^{(3)}$ is the triplet correlation entropy and so on. At densities near the melting point we propose that $S^{(2)}$ and $S^{(3)}$ should be defined as

$$S^{(2)} = -\frac{1}{2}\rho \int g^{(2)}(r) \ln g^{(2)}(r) dr, \quad (2)$$

and

$$S^{(3)} = -\frac{1}{6}\rho^2 \iiint g^{(3)}(r, s, t) \ln g^{(3)}(r, s, t) dr ds dt, \quad (3)$$

where $g^{(2)}$ and $g^{(3)}$ are the pair and triplet correlation functions and $r = |\mathbf{r}| = |\mathbf{r}_2 - \mathbf{r}_1|$, $s = |\mathbf{s}| = |\mathbf{r}_3 - \mathbf{r}_1|$ and $t = |\mathbf{s} - \mathbf{r}|$. The irreducible part of the triplet correlation function is defined by

$$\delta g^{(3)}(r, s, t) = g^{(3)}(r, s, t) / (g^{(2)}(r)g^{(2)}(s)g^{(2)}(t)). \quad (4)$$

Throughout this paper the entropy, as usual, is expressed in units of k_B per particle. We removed the second integrals from eqs. (2) and (3) in Ref. 1). As mentioned in Ref. 1), the excess entropy (*i.e.*, ion configurational entropy) S_E is given as

$$S_E = S^{(2)} + S^{(3)} + S^{(x)}. \quad (5)$$

3. Results and Discussion

We recalculated $S^{(2)}$ and $S^{(3)}$ using the same approximations given in Ref. 1). Numerical results of the entropy calculations, based on the newly defined $S^{(2)}$ and $S^{(3)}$, are summarized in Table 1. As seen from the table, both the total entropy S_{total} and $S^{(2)} + S^{(3)}$ are in good agreement with experimental values. Obviously, the values of $S^{(x)}$ are virtually zero (within error bars) for Li, Na, K, Rb, Cs and Al, and are negligibly small for Cu and Mg. For Pb, however, $S^{(x)}$ has a non-negligible contribution but is *negative* in sign as expected. Graphical comparison is made in Fig. 1 for the total

Table 1 Correlation and total entropies obtained from the diffraction data. $S^{(x)}$ denotes a contribution arising from the four-body and higher-order correlations, which is estimated by $S_E(\text{expt}) - (S^{(2)} + S^{(3)})$. Errors in $S^{(2)} + S^{(3)}$ are of order ± 0.05 at best for Li, Na, K, Rb, Cs, Mg and Al, but ± 0.1 for Cu and Pb (see Refs. 1), 5)). Experimental values of S_{total} are taken from Hultgren *et al.*⁶⁻¹⁴⁾ and theoretical values of S_{total} are obtained from $S_{\text{PG}} + S^{(2)} + S^{(3)} + S_{\text{elec}}$ (see eqs. (19) and (20) in Ref. 1) for S_{PG} and S_{elec} , respectively).

	T (K)	ρ (10^3 kg m^{-3})	$S^{(2)} (Nk_B)$	$S^{(3)} (Nk_B)$	$S^{(2)} + S^{(3)} (Nk_B)$	$S_E (Nk_B)$	$S^{(x)} (Nk_B)$	$S_{\text{total}} (Nk_B)$	
			calc	calc	calc	expt	calc	calc	expt
Li	463	0.512	-2.49	-1.01	-3.50	-3.44	0.06	5.68	5.74
Na	378	0.928	-2.57	-0.99	-3.56	-3.46	0.10	7.74	7.84
K	343	0.826	-2.42	-0.95	-3.37	-3.47	-0.10	9.24	9.14
Rb	313	1.476	-2.59	-1.00	-3.59	-3.59	0.00	10.27	10.27
Cs	303	1.836	-2.52	-1.06	-3.58	-3.57	0.01	11.13	11.14
Cu	1423	7.947	-2.80	-0.79	-3.59	-3.44	0.15	10.13	10.28
Mg	953	1.58	-2.46	-0.74	-3.20	-3.38	-0.18	9.19	9.01
Al	943	2.383	-2.66	-0.82	-3.48	-3.55	-0.07	8.70	8.63
Pb	613	10.68	-2.60	-0.89	-3.49	-3.94	-0.45	11.64	11.19

Table 2 D , η and γ of liquid alkali, noble and typical polyvalent metals calculated from the diffraction data. Experimental data are taken from Ref. 1).

	T (K)	σ (10^{-10} m)	$g(\sigma)$	$D(10^{-9} \text{ m}^2 \text{ s}^{-1})$		$\eta (\text{mPa s})$		$\gamma (\text{Nm}^{-1})$	
				calc	expt	calc	expt	calc	expt
Li	463	3.0	2.484	7.01	5.98–6.80	0.484	0.602	0.338	0.398
Na	378	3.7	2.424	4.03	3.85–4.23	0.56	0.70	0.193	0.191
K	343	4.6	2.351	4.33	3.59–3.76	0.38	0.54	0.096	0.115
Rb	313	4.8	2.468	2.28	2.22–2.68	0.627	0.674	0.103	0.085
Cs	303	5.1	2.583	1.94	2.16–2.31	0.674	0.686	0.087	0.070
Cu	1423	2.5	2.755	3.35	3.18–3.97	3.73	3.5	1.509	1.303
							4.34		1.37
Mg	953	3.1	2.463	7.20	5.63 [#]	0.938	1.25	0.502	0.559
Al	943	2.8	2.829	5.34	4.87 ⁺	1.39	1.2–4.2	0.701	0.914
Pb	613	3.3	3.073	1.88	1.68–2.19	2.13	2.61	0.310	0.458

[#]Predicted at 923 K, ⁺Predicted at 933 K.

Fig. 1 Comparison between the theory and the experiment for total entropy S_{total} near the melting point. The solid line denotes the 45° axis.

Fig. 2 Comparison between the theory and the experiment for diffusion coefficient D near the melting point: Present work ($\times$), Ref. 1 ($\bullet$). The solid line denotes the 45° axis.

entropy.

On the other hand, the physical properties of liquid metals derived from $S^{(2)} + S^{(3)}$ are given in Table 2, and are displayed in Figs. 2–4 for comparison with the experimental values. All the recalculated results are very much the same as those obtained in the previous paper.¹⁾

4. Conclusion

In summary, using the newly defined $S^{(2)}$ and $S^{(3)}$, we can avoid the large positive values of $S^{(x)}$. Our proposed method is easier in the calculation of the entropy and more reasonable

Fig. 3 Same as Fig. 2, but for viscosity coefficient η .

Fig. 4 Same as Fig. 2, but for surface tension γ .

in the interpretation of $S^{(x)}$ than the original formulation by Baranyai and Evans.

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