LETTERS TO THE EDITOR

Effect of Softness of Interatomic Forces on Entropies of Liquid Metals near the Melting Point

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When a liquid metal structure factor is of hard sphere form, there is a correlation between the structure factor and the entropy. The theory relating the thermodynamics of a real liquid to that of a hard sphere reference system is well reviewed, for example, by Young⁽¹⁾ in Bristol conference. The extent to which this correlation exists in liquid metals is investigated by Young and coworkers by comparing, for each system and at various temperatures, the packing fractions deduced respectively from entropy and structure factor measurements. However, it was difficult to establish a rule describing the relationship between entropies and structure factors of liquid metals.

The purpose of the present letter is to show a useful correlation by considering the effect of the softness of the interatomic forces on entropies near the melting point. The motivation to do this research comes from our recent work⁽²⁾ on correlation entropies of liquid rare earth metals near the melting point. In that work the excess entropy of ion disorder alone, S_E , is given by

$$S_E = S^{(2)} + S^{(3)} + \dots = S_{\text{pack}} + S_s \quad (1)$$

where $S^{(2)}$ and $S^{(3)}$ are, respectively, the pair and triplet correlation entropy. S_{pack} is the excess entropy due to the finite packing of the hard spheres, best described via the negative Carnahan-Starling expression⁽³⁾

$$S_{\text{pack}} = -\frac{\eta(4-3\eta)}{(1-\eta)^2} \quad (2)$$

Here η is the packing fraction defined by $\eta = \pi n \sigma^3 / 6$, n and σ being the number density and the effective hard sphere diameter, respectively. S_s is an entropy contribution arising from the softness of the interatomic forces. Young⁽¹⁾ concluded that S_s is always positive, but he did not provide this contribution explicitly for each metal. The key to solve the problem lies in the size of S_s . Recently we became aware of the paper of Bari *et al.*⁽⁴⁾ in which the effect of the soft force part to the entropy is discussed

in the light of thermodynamic perturbation theory. An explicit expression of the soft force contribution to the entropy is given by

$$S_s / Nk_B = \pi n f(\sigma_0 - \sigma_m)(T / T_m)^{1/2} \sigma^2 g_0(\sigma), \quad (3)$$

where, σ_0 is the location of the minimum in the pair potential, σ_m refers to the melting point, T_m . Here $\sigma_0 = 1.0878(n_m)^{-1/3}$ as given by Protopapas *et al.*⁽⁵⁾ and n_m refers to the number density at the melting point. $g_0(\sigma)$ is the hard sphere pair correlation function at the core and is given by

$$g_0(\sigma) = \frac{1 - \eta/2}{(1 - \eta)^3} \quad (4)$$

using Carnahan-Starling formula. f is a parameter related to the soft force part of the pair potential and is approximated as ~ 0.35 for all systems at all temperatures. For details of derivation of eq. (3) please see Ref. (4). Therefore the total entropy, S , of the system (in units of k_B per ion) is given by⁽¹⁾⁽²⁾

$$S = S_{\text{PG}} + S_{\text{elec}} + S_{\text{pack}} + S_s, \quad (5)$$

where S_{PG} is the perfect gas entropy and S_{elec} the electron excitation entropy. For liquid rare earth metals a magnet-

Table 1 The entropies of the liquid rare earth metals near the melting point (in units of Nk_B). The values of η are taken from Ref. (6) but those for Pr and Nd are from Ref. (7). The values of S_{PG} , S_{elec} , S_{mag} , S_{pack} and S_{expt} are due to Ref. (2).

	T/K	η	S_{PG}	S_{elec}	S_{mag}	S_{pack}	S_s	S_{calc}	S_{expt}	$S_{\text{calc}}/S_{\text{expt}}$
La	1243	0.43	15.7	0.5	0	-3.6	0.5	13.1	13.0	1.01
Ce	1143	0.42	15.5	0.6	1.8	-3.4	0.5	15.0	14.4	1.04
Pr	1223	0.43	15.6	0.4	2.2	-3.6	0.5	15.1	15.8	0.96
Nd	1323	0.43	15.7	0.5	2.3	-3.6	0.5	15.4	15.9	0.97
Eu	1103	0.42	16.0	0.3	2.1	-3.4	0.5	15.5	15.6	0.99
Gd	1603	0.43	16.2	1.0	2.1	-3.6	0.5	16.2	15.6	1.04
Tb	1653	0.43	16.2	1.1	2.6	-3.6	0.5	16.8	16.8	1.00
Yb	1123	0.43	16.0	0.3	0	-3.6	0.5	13.2	13.0	1.02

Table 2 The entropies of the liquid 3d transition metals near the melting point (in units of Nk_B). The values of η are taken from Ref. (6). The values of S_{PG} , S_{el}^s , S_{el}^d and S_{expt} are from Ref. (8) ($S_{elec} = S_{el}^s + S_{el}^d$).

	T/K	η	S_{PG}	S_{el}^s	S_{el}^d	S_{pack}	S_s	S_{calc}	S_{expt}	S_{calc}/S_{expt}
Ti	1973	0.44	14.06	0.38	0.92	-3.76	0.54	12.14	12.01	1.01
V	2173	0.44	14.10	0.37	0.91	-3.76	0.53	12.15	12.08	1.01
Cr	2173	0.45	14.00	0.33	0.94	-3.94	0.57	11.90	11.58	1.03
Mn	1533	0.45	13.66	0.25	0.78	-3.94	0.57	11.32	12.05	0.94
Fe	1833	0.44	13.84	0.27	1.08	-3.76	0.53	11.96	12.07	0.99
Co	1823	0.45	13.84	0.27	1.19	-3.94	0.57	11.93	12.08	0.99
Ni	1773	0.45	13.79	0.26	1.33	-3.94	0.57	12.01	11.72	1.02
Ni	1773	0.46	13.79	0.26	1.33	-4.15	0.61	11.84	11.72	1.01

ic contribution, S_{mag} , must be added to eq. (5). Explicit expressions of S_{PG} , S_{elec} and S_{mag} are given in Refs. (1) and (2). Using eqs.(2), (3) and (5) we can now estimate the total entropy, S , and compare this with the experimental data. Numerical results are summarized in **Table 1** for eight liquid rare earth metals studied in Ref. (2). On comparing column 9 with column 10, agreement between theory and experiment seems to be quite good. **Table 2** displays the results of liquid 3d transition metals near the melting point⁽⁸⁾. Agreement of S_{calc} with S_{expt} is surprisingly good. In order to see how S_{calc} depends on the size of η , we tried the case of $\eta=0.46$ for Ni. A better agreement between S_{calc} and S_{expt} is obtained for this choice of η , though the value of 0.45 is listed in **Table 3-1** of Ref. (6). Finally, we examined liquid alkali metals and typical polyvalent metals near the melting point. The results are shown in Table 3. From comparison of S_{calc} with S_{expt} , it is seen that agreement between the two is excellent. So far, we took no account of experimental errors which might be contained in S_{expt} . Typically, entropies are quoted by Hultgren *et al.*⁽⁹⁾ to an accuracy of $\pm 0.02k_B \sim \pm 0.2k_B$ per ion for alkali, polyvalent and 3d transition metals, and $\pm 0.04k_B \sim \pm 1.0k_B$ per ion for rare earth metals. Even if observed entropies are not very accurate, we believe that the story mentioned above is absolutely true for the entropy analysis.

Table 3 The entropies of the liquid simple metals near the melting point (in units of Nk_B). The values of η are taken from Ref. (6) but those for Rb, Cs, Al and Bi are taken from Ref. (4). Experimental data, S_{expt} , are due to Hultgren *et al.*⁽⁹⁾

	T/K	η	S_{PG}	S_{elec}	S_{pack}	S_s	S_{calc}	S_{expt}	S_{calc}/S_{expt}
Li	463	0.46	9.14	0.04	-4.13	0.61	5.66	5.74	0.99
Na	378	0.46	11.25	0.05	-4.13	0.61	7.78	7.84	0.99
K	343	0.46	12.54	0.07	-4.13	0.61	9.09	9.14	0.99
Rb	313	0.46	13.78	0.08	-4.13	0.57	10.30	10.27	1.00
Cs	303	0.46	14.62	0.09	-4.13	0.60	11.18	11.14	1.00
Cu	1423	0.46	13.63	0.09	-4.13	0.62	10.21	10.28	0.99
Mg	953	0.46	12.24	0.12	-4.13	0.61	8.84	9.02	0.98
Al	943	0.46	12.07	0.11	-4.13	0.60	8.65	8.63	1.00
Pb	600.6	0.46	14.99	0.11	-4.13	0.52	11.49	11.13	1.03
Bi	573	0.46	15.00	0.12	-4.13	0.62	11.61	11.46	1.01

In summary, theoretical hard-sphere structure factors with the packing fractions given in Tables 1–3 describe experimental structure factor data quite well. The same values of the packing fractions describe quite well entropies near the melting point.

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